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Essential Graduate Physics
Lecture Notes and Problems

Beta version

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Part SM: Statistical Mechanics

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Chapter 1. Review of Thermodynamics

This chapter starts from a brief discussion of the subject of statistical physics and thermodynamics, and the relation between these two disciplines. Then I proceed to a review of the basic notions and relations of thermodynamics. Most of this material is supposed to be known to the reader from his or her undergraduate studies,¹ so the discussion is rather brief.

1.1. Introduction: Statistical physics and thermodynamics

Statistical physics (alternatively called “statistical mechanics”) and *thermodynamics* are two different approaches to the same goal: a description of internal dynamics of large physical systems, notably those consisting of many, $N \gg 1$, identical particles – or other components. The traditional example of such a system is a human-scale portion of a gas, with the number N of molecules of the order of the Avogadro number $N_A \sim 10^{23}$.² The “internal dynamics” is an (admittedly loose) term meaning all the physics unrelated to the motion of the system as a whole. The most important example of the internal dynamics is the thermal motion of atoms and molecules.

The motivation for the statistical approach to such systems is straightforward: even if the laws governing the dynamics of each particle and their interactions were exactly known, and we had infinite computing resources at our disposal, calculating the exact evolution of the system in time would be impossible, at least because it is completely impracticable to measure the exact initial state each component, e.g., the initial position and velocity of each particle. The situation is further exacerbated by the phenomena of chaos and turbulence,³ and the quantum-mechanical uncertainty,⁴ which do not allow the exact calculation of final positions and velocities of the component particles even if their initial state is known with the best possible precision. As a result, in most situations only statistical predictions about behavior of such systems may be made, with the *probability theory* becoming a major part of the mathematical tool arsenal.

However, the statistical approach is not as bad as it may look. Indeed, it is almost self-evident that any measurable *macroscopic* variable characterizing a stationary system of $N \gg 1$ particles as a whole (think, e.g., about pressure P of a gas contained in a fixed volume V) is almost constant in time. Indeed, we will see below that, besides certain exotic exceptions, the relative fluctuations – either in time, or among macroscopically similar systems - of such a variable are of the order of $1/\sqrt{N}$, i.e. for $N \sim N_A$ are extremely small. As a result, the *average values* of macroscopic variables may characterize the state of the system rather well. Their calculation is the main task of statistical physics. (Though the analysis of fluctuations is also an important task, but due to the fluctuation smallness, the analysis in most cases may be based on perturbative approaches – see Chapter 5.)

¹ For remedial reading, I can recommend, for example (in the alphabetical order): C. Kittel and H. Kroemer, *Thermal Physics*, 2nd ed., W. H. Freeman (1980); F. Reif, *Fundamentals of Statistical and Thermal Physics*, Waveland (2008); D. V. Schroeder, *Introduction to Thermal Physics*, Addison Wesley (1999).

² See, e.g., Sec. 4 below. (Note that in these notes, the chapter number is dropped in references to figures, formulas, and sections within the same chapter.)

³ See, e.g., CM Chapters 8 and 9. (Acronyms CM, EM, and QM refer to other of my lecture note series.)

⁴ See, e.g., QM Chapter 1.

Let us have a look at typical macroscopic variables the statistical physics and thermodynamics should operate with. Since I have already mentioned pressure P and volume V , let me start with this famous pair. First of all, note that volume is an *extensive variable*, i.e. a variable whose value for a system consisting of several non-interacting (or weakly interacting) parts is the sum of those of its parts. On the other hand, pressure is an example of *intensive variables* whose value is the same for different parts of a system - if they are in equilibrium. In order to understand why P and V form a natural pair of variables, let us consider the classical playground of thermodynamics, a portion of a gas contained in a cylinder, closed with a movable piston of area A (Fig. 1). Neglecting friction between the walls and the piston, and assuming that it is being moved slowly enough (so that the pressure P , at any instant, is virtually the same for all parts of the volume), the elementary work of the external force $\mathcal{F} = -PA$, compressing the gas, at a small piston displacement dx , is

$$d\mathcal{W} = \mathcal{F}dx = \left(\frac{\mathcal{F}}{A}\right)(Adx) = -PdV. \quad (1.1) \quad \text{Work on a gas}$$

It is clear that the last expression is more general than the model shown in Fig. 1, and does not depend on the particular shape of the system surface.⁵

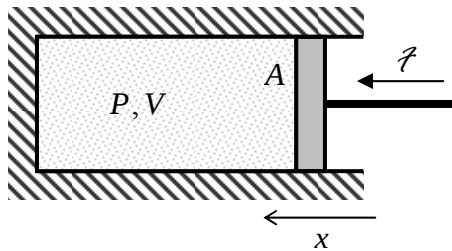


Fig. 1.1. Compressing a gas.

From the point of analytical mechanics,⁶ V and $(-P)$ is just one of many possible canonical pairs of generalized coordinates q_j and generalized forces $\mathcal{F}_j$, whose products $d\mathcal{W}_j = -\mathcal{F}_j dq_j$ give contribution to the total work of the environment on the system under analysis. For example, the reader familiar with the basics of electromagnetism knows that the elementary work of an electric field on a unit volume of a media is⁷

$$d\mathcal{W} = \mathcal{E} \cdot d\mathcal{D} = \sum_{j=1}^3 \mathcal{E}_j d\mathcal{D}_j, \quad (1.2)$$

so that the role of generalized coordinates is played by Cartesian components of the electric displacement $\mathcal{D}$, while the components of the electric field $\mathcal{E}$ serve as the corresponding generalized forces. Similarly, the elementary work of the magnetic field $\mathcal{H}$ is⁸

⁵ In order to prove that, it is sufficient to integrate the scalar product $d\mathcal{W} = d\mathcal{F} \cdot d\mathbf{r}$, with $d\mathcal{F} = -P\mathbf{n}d^2r$, where $d\mathbf{r}$ is the surface displacement vector (see, e.g., CM Sec. 7.1), and $\mathbf{n}$ is the outer normal, over the surface.

⁶ See, e.g., CM Chapters 2 and 10.

⁷ See, e.g., EM Eq. (3.82).

⁸ See, e.g., EM Eq. (5.128). Note that Eqs. (2)-(3) are in SI units (used throughout this lecture series). In the Gaussian units, the right-hand parts of these relations have additional coefficients $1/4\pi$.

$$d\mathcal{W} = \mathcal{H} \cdot d\mathcal{B} = \sum_{j=1}^3 \mathcal{H}_j d\mathcal{B}_j, \quad (1.3)$$

where $\mathcal{B}$ is the magnetic induction. This list may be extended to other interactions (such as gravitation, surface tension in fluids, etc.). Following tradition, I will use the $\{-P, V\}$ pair in almost all the formulas below, as well in most instances but the reader should remember that they all are valid for any other pair $\{\mathcal{A}_j, q_j\}$.

Again, the specific relations between the variables of each pair listed above are typically affected by the statistics of the components (particles) of a body, but their definition is not based on statistics. The situation is very different for a very specific pair of variables, *temperature* T and *entropy* S , although these “sister variables” participate in many formulas of thermodynamics exactly like one more canonical pair $\{\mathcal{A}_j, q_j\}$. However, the very existence of these two variables is due to statistics. Temperature T is an intensive variable that characterizes the degree of thermal “agitation” of system components. On the contrary, entropy S is an extensive variable that in most cases evades immediate perception by human senses; it is a qualitative measure of *disorder* of the system, i.e. the degree of our ignorance about its exact microscopic state.⁹

The reason for the appearance of the $\{T, S\}$ pair of variables in formulas is that the statistical approach to large systems of particles brings some qualitatively new results, most notably the notion of *irreversible* time evolution of collective (*macroscopic*) variables describing the system. On one hand, such irreversibility looks absolutely natural in such phenomena as the diffusion of an ink drop in a glass of water. In the beginning, the ink molecules are located in a certain small part of system’s volume, i.e. to some extent ordered, while at the late stages of diffusion, the position of each molecule is essentially random. However, as a second thought, the irreversibility is rather surprising,¹⁰ taking into account that it takes place even if the laws governing the motion of system’s components are *time-reversible* – such as the Newton laws or the basic laws of quantum mechanics. Indeed, if, at a late stage of the diffusion process, we exactly reversed the velocities of all molecules simultaneously, the ink molecules would again gather (for a moment) into the original spot.¹¹ The problem is that getting the *information* necessary for the exact velocity reversal is not practicable. This example shows a deep connection between the statistical mechanics and the information theory.

A qualitative discussion of the reversibility-irreversibility dilemma requires a strict definition of the basic notion of statistical mechanics (and indeed the probability theory), the *statistical ensemble*, and I would like to postpone it until the beginning of Chapter 2. In particular, in that chapter we will see that the basic law of irreversible behavior is the increase of entropy S in any closed system. Thus, statistical mechanics, without defying the “microscopic” laws governing evolution of system’s components,

⁹ The notion of entropy was introduced into thermodynamics in the 1850s by R. Clausius, on the background of an earlier pioneering work by S. Carnot (see Sec. 7 below), as a variable related to “useful thermal energy” rather than a measure of disorder. In the absence of any clue of entropy’s microscopic origins (which had to wait for decades until the works by L. Boltzmann and J. Maxwell), this was an amazing intellectual achievement.

¹⁰ Indeed, as recently as in the late XIX century, the very possibility of irreversible macroscopic behavior of microscopically reversible systems was questioned by some serious scientists, notably by J. Loschmidt in 1876.

¹¹ While quantum-mechanical effects, with their intrinsic uncertainty, are quantitatively important in this example, our qualitative discussion does not depend on them. A good example is the chaotic, but classical motion of a billiard ball on a 2D Sinai table – see CM Fig. 9.8.

introduces on top of them some new “macroscopic” laws, intrinsically related to the evolution of *information*, i.e. the degree of our knowledge of the microscopic state of the system.

To conclude this brief discussion of variables, let me mention that as in all fields of physics, a very special role in statistical mechanics is played by *energy* E . In order to emphasize the commitment to disregard the motion of the system as a whole, in thermodynamics it is frequently called the *internal energy*, though for brevity, I will mostly skip the adjective. Its simplest example is the kinetic energy of the thermal motion of molecules in a dilute gas, but in general E also includes not only the individual energies of all system’s components, but also their interactions with each other. Besides a few pathological cases of very-long-range interactions (such as the Coulomb interactions in plasma with uncompensated charge density), the interactions may be treated as local; in this case the internal energy is proportional to N , i.e. is an extensive variable. As will be shown below, other extensive variables with the dimension of energy are often very useful, including the (Helmholtz) *free energy* F , the *Gibbs energy* G , *enthalpy* H , and *grand potential* Ω . (The collective name for such variables is *thermodynamic potentials*.)

Now, we are ready for a brief discussion of the relation between *statistical physics* and *thermodynamics*. While the task of statistical physics is to calculate the macroscopic variables discussed above,¹² using this or that particular microscopic model of the system, the main role of thermodynamics is to derive some general relations between the average values of the macroscopic variables (called *thermodynamic variables*) that do not depend on specific models. Surprisingly, it is possible to accomplish such a feat using a few either evident or very plausible general assumptions (sometimes called the *laws of thermodynamics*), which find their proof in statistical physics.¹³ Such general relations allow us to reduce rather substantially the amount of calculations we have to do in statistical physics; in many cases it is sufficient to calculate from statistics just one or two variables, and then use thermodynamic relations to calculate all other properties of interest. Thus the thermodynamics, sometimes snubbed at as a phenomenology, deserves every respect not only as a discipline which is, in a certain sense, more general than statistical physics as such, but also as a very useful science. This is why the balance of this chapter is devoted to a brief review of thermodynamics.

1.2. The 2nd law of thermodynamics, entropy, and temperature

Thermodynamics accepts a phenomenological approach to entropy S , postulating that there is such a unique extensive measure of disorder, and that in a *closed system*,¹⁴ it may only grow in time, reaching its constant (maximum) value at equilibrium.¹⁵

$$dS \geq 0. \quad (1.4)$$

2nd law of
thermo-
dynamics

This postulate is called the 2nd law of thermodynamics – arguably its only substantial new law.

¹² Several other quantities, for example the heat capacity C , may be obtained as partial derivatives of the basic variables discussed above. Also, at certain conditions, the number of particles N in the system is not fixed and may be also considered as an (extensive) variable.

¹³ Admittedly, some of these proofs are based on other (but deeper) postulates, for example the central statistical hypothesis – see Sec. 2.2.

¹⁴ Defined as a system completely isolated from the environment, i.e. the system with its internal energy fixed.

¹⁵ Implicitly, this statement also postulates the existence, in a closed system, of *thermodynamic equilibrium*, an asymptotically reached state in which all thermodynamic variables, including entropy, remain constant.

Surprisingly, this law, together with the additivity of S in composite systems of non-interacting parts (as an extensive variable), is sufficient for a formal definition of temperature, and a derivation of its basic properties that comply with our everyday notion of this variable. Indeed, let us consider a particular case: a closed system consisting of two fixed-volume subsystems (Fig. 2) whose internal relaxation is very fast in comparison with the rate of the thermal flow (i.e. the energy and entropy exchange) between the parts. In this case, on the latter time scale, each part is always in some quasi-equilibrium state, which may be described by a unique relation $E(S)$ between its energy and entropy.¹⁶

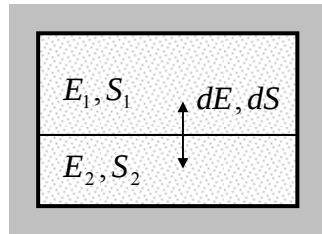


Fig. 1.2. Composite thermodynamic system.

Neglecting the interaction energy between the parts (which is always possible at $N \gg 1$, in the absence of long-range interactions), we may use the extensive character of variables E and S to write

$$E = E_1(S_1) + E_2(S_2), \quad S = S_1 + S_2, \quad (1.5)$$

for the full energy and entropy of the system. Now let us calculate the following derivative:

$$\frac{dS}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2} \frac{dE_2}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2} \frac{d(E - E_1)}{dE_1}. \quad (1.6)$$

Since the total energy E of the system is fixed and hence independent of its re-distribution between the sub-systems, $dE/dE_1 = 0$, and we get

$$\frac{dS}{dE_1} = \frac{dS_1}{dE_1} - \frac{dS_2}{dE_2}. \quad (1.7)$$

According to the 2nd law of thermodynamics, when the two parts reach the thermodynamic equilibrium, the total entropy S reaches its maximum, so that $dS/dE_1 = 0$, and Eq. (7) yields

$$\frac{dS_1}{dE_1} = \frac{dS_2}{dE_2}. \quad (1.8)$$

Thus we see that if a thermodynamic system may be partitioned into weakly interacting macroscopic parts, their derivatives dS/dE should be equal in the equilibrium. The reciprocal of such derivative is called *temperature*. Taking into account that our analysis pertains to the situation (Fig. 2) when both volumes $V_{1,2}$ are fixed, we may write this definition as

$$\left(\frac{\partial E}{\partial S} \right)_V \equiv T, \quad (1.9)$$

Definition of
temperature

¹⁶ Here we strongly depend on a very important (and possibly the least intuitive) aspect of the 2nd law, namely that the entropy is the *unique* measure of disorder, i.e. its only measure which may affect the system's energy, or any other thermodynamic variable.

subscript V meaning that volume is kept constant at differentiation. (Such notation is common and very useful in thermodynamics, with its broad range of variables.)

Note that according to Eq. (9), if temperature is measured in energy units (as I will do in this course for the brevity of notation), S is dimensionless.¹⁷ The transfer to the SI or Gaussian units, i.e. to temperature T_K measured in kelvins (not “Kelvins”, not “degrees Kelvin”, please!), is given by relation $T = k_B T_K$, where the *Boltzmann constant* $k_B \approx 1.38 \times 10^{-23} \text{ J/K} = 1.38 \times 10^{-16} \text{ erg/K}$.¹⁸ In these units, the entropy becomes dimensional: $S_K = k_B S$.

The definition of temperature, given by Eq. (9), is of course in a sharp contrast with the popular notion of T as a measure of the average energy per particle. However, as we will repeatedly see below, in most cases these two notions may be reconciled. In particular, let us list some properties of T , which are in accordance with our everyday notion of temperature:

- (i) according to Eq. (9), temperature is an intensive variable (since both E and S are extensive), i.e., in a system of similar particles, independent of the particle number N ;
- (ii) temperatures of all parts of a system are equal at equilibrium – see Eq. (8);
- (iii) in a closed system whose parts are *not* in equilibrium, thermal energy (*heat*) always flows from a warmer part (with higher T) to the colder part.

In order to prove the last property, let us come back to the closed, composite system shown in Fig. 2, and consider another derivative:

$$\frac{dS}{dt} = \frac{dS_1}{dt} + \frac{dS_2}{dt} = \frac{dS_1}{dE_1} \frac{dE_1}{dt} + \frac{dS_2}{dE_2} \frac{dE_2}{dt}. \quad (1.10)$$

If the internal state of each part is very close to equilibrium (as was assumed from the very beginning) at each moment of time, we can use Eq. (9) to replace derivatives $dS_{1,2}/dE_{1,2}$ for $1/T_{1,2}$ and get

$$\frac{dS}{dt} = \frac{1}{T_1} \frac{dE_1}{dt} + \frac{1}{T_2} \frac{dE_2}{dt}. \quad (1.11)$$

Since in a closed system $E = E_1 + E_2 = \text{const}$, these time derivatives are related as $dE_2/dt = -dE_1/dt$, and Eq. (11) yields

$$\frac{dS}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \frac{dE_1}{dt}. \quad (1.12)$$

But in accordance with the 2nd law of thermodynamics, the derivative cannot be negative: $dS/dt \geq 0$. Hence,

$$\left(\frac{1}{T_1} - \frac{1}{T_2} \right) \frac{dE_1}{dt} \geq 0. \quad (1.13)$$

¹⁷ Here I have to mention a traditional unit of energy, still used in some fields related to thermodynamics: the *calorie*; in the most common definition (the so-called *thermochemical calorie*) it equals exactly 4.148 J.

¹⁸ For more exact value of this and other constants, see appendix CA: *Selected Physical Constants*. Note that both T and T_K define the *absolute* (also called “thermodynamic”) *scale* of temperature, in contrast to such artificial temperature scales as degrees Celsius (“centigrades”), defined as $T_C \equiv T_K + 273.15$, or degrees Fahrenheit: $T_F \equiv (9/5)T_C + 32$.

For example, if $T_1 > T_2$ (i.e. $1/T_1 < 1/T_2$), then $dE_1/dt \leq 0$, i.e. the warmer part gives energy to its colder counterpart.

Note also that at such a heat exchange, at fixed volumes $V_{1,2}$, and $T_1 \neq T_2$, increases the total system entropy, without performing any “useful” mechanical work.

1.3. The 1st and 3rd laws of thermodynamics, and heat capacity

Now let us consider a *thermally insulated* system whose volume V may be changed by a deterministic force – see, for example, Fig. 1. Such system is different from the fully closed one, because its energy E may be changed by the external force’s work – see Eq. (1):

$$dE = d\mathcal{W} = -PdV. \quad (1.14)$$

Let the volume change be so slow ($dV/dt \rightarrow 0$) that the system is virtually at equilibrium at any instant without much error. Such a slow process is called *reversible*, and in this particular case of a thermally insulated system, it is also called *adiabatic*. If pressure P (or any a generalized external force $\mathcal{F}_j$) is deterministic, i.e. is a predetermined function of time independent on the state of the system under analysis, it may be considered as coming from a fully ordered system, i.e. the one having zero entropy, with the total system completely closed. Since according to the second of Eqs. (5), the entropy of the total closed system should stay constant, S of the system under analysis should stay constant on its own. Thus we arrive at a very important conclusion: an adiabatic process, the entropy of a system cannot change.¹⁹ This means that we can use Eq. (14) to write

$$P = -\left(\frac{\partial E}{\partial V}\right)_S. \quad (1.15)$$

Let us now consider an even more general thermodynamic system that may also exchange thermal energy (“heat”) with the environment (Fig. 3).

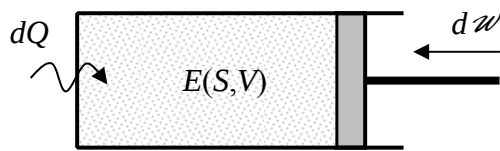


Fig. 1.3. General thermodynamic process involving both the mechanical work and heat exchange with the environment.

For such a system, our previous conclusion about the entropy constancy is not valid, so that S , in equilibrium, may be a function of not only energy E , but also of volume V . Let us resolve this relation for energy: $E = E(S, V)$, and write the general mathematical expression for the full differential of E as a function of these two independent arguments:

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV. \quad (1.16)$$

¹⁹ A general (not necessarily adiabatic) process conserving entropy is sometimes called *isentropic*.

This formula, based on the stationary relation $E = E(S, V)$, is evidently valid not only in equilibrium, but also for very slow, reversible²⁰ processes. Now, using Eqs. (9) and (15), we may rewrite Eq. (16) as

$$dE = TdS - PdV. \quad (1.17) \quad \text{Energy: differential}$$

The second term in the right-hand part of this equation is just the work of the external force, so that due to the conservation of energy,²¹ the first term has to be equal to the *heat* dQ transferred from the environment to the system (see Fig. 3):

$$dE = dQ + d\mathcal{W}, \quad (1.18) \quad \text{1st law of thermo-}$$

$$dQ = TdS. \quad (1.19) \quad \text{dynamics}$$

The last relation, divided by T and then integrated along an arbitrary (but reversible!) process,

$$S = \int \frac{dQ}{T} + \text{const}, \quad (1.20)$$

is sometimes used as an alternative definition of entropy S - provided that temperature is defined not by Eq. (9), but in some independent way. It is useful to recognize that entropy (like energy) may be defined to an arbitrary constant, which does not affect any other thermodynamic observables. The common convention is to take

$$S \rightarrow 0 \text{ at } T \rightarrow 0. \quad (1.21)$$

This condition is sometimes called the *3rd law of thermodynamics*, but it is important to realize that this is just a convention rather than a real law.²² Indeed, the convention corresponds well to the notion of the full order at $T = 0$ in some systems (e.g., perfect crystals), but creates ambiguity for other systems, e.g., amorphous solids (like the usual glasses) that may remain, for “astronomic” times, highly disordered even at $T \rightarrow 0$.

Now let us discuss the notion of *heat capacity* that, by definition, is the ratio dQ/dT , where dQ is the amount of heat that should be given to a system to raise its temperature by a small amount dT .²³ (This notion is very important, because it may be most readily measured experimentally.) The heat capacity depends, naturally, on whether the heat dQ goes only into an increase of the internal energy dE

²⁰ Let me emphasize that an adiabatic process is reversible, but not vice versa.

²¹ Such conservation, expressed by Eqs. (18)-(19), is sometimes called the *1st law of thermodynamics*. While it (in contrast with the 2nd law) does not present any new law of nature on the top of mechanics, and in particular was already used de-facto to write the first of Eqs. (5) and Eq. (14), such grand name was quite justified in the mid-19th century when the mechanical nature of the internal energy (thermal motion) was not at all clear. In this context, the names of two great scientists, J. von Mayer (who was first to conjecture the conservation of the sum of the thermal and macroscopic mechanical energies in 1841), and J. Joule (who proved the conservation experimentally two years later), have to be reverently mentioned.

²² Actually, the 3rd law (also called the *Nernst theorem*) as postulated by W. Nernst in 1912 was different - and really meaningful: “It is impossible for any procedure to lead to the isotherm $T = 0$ in a finite number of steps.” I will discuss this postulate in the end of Sec. 6.

²³ By this definition, the full heat capacity of a system is an *extensive* variable. The capacity per either unit mass or per particle (i.e., an *intensive* variable), is called the *specific heat capacity* or just the *specific heat*. Note, however, that in some texts, the last term is used for the heat capacity of the system as the whole as well, so that some caution is in order.

of the system (as it does if volume V is constant), or also into the mechanical work ($-d\mathcal{W}$) that may be performed at expansion - as it happens, for example, if pressure P , rather than volume V , is fixed (the so-called *isobaric* process – see Fig. 4).²⁴

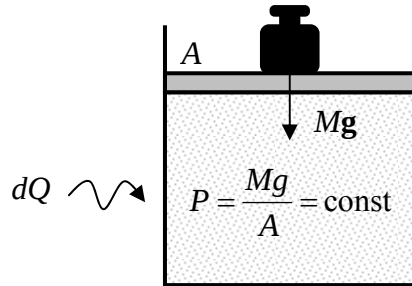


Fig. 1.4. The simplest implementation of an isobaric process.

Hence we should discuss two different quantities, the *heat capacity at fixed volume*,

$$C_V \equiv \left(\frac{\partial Q}{\partial T} \right)_V \quad (1.22)$$

Heat
capacity
definitions

and *heat capacity at fixed pressure*

$$C_P \equiv \left(\frac{\partial Q}{\partial T} \right)_P, \quad (1.23)$$

and expect that for all “normal” (mechanically stable) systems, $C_P \geq C_V$. The difference between C_P and C_V is rather minor for most liquids and solids, but may be very substantial for gases – see Sec. 4.

1.4. Thermodynamic potentials

A technical disadvantage of Eqs. (22) and (23) is that ∂Q is not a differential of a function of state of the system,²⁵ and hence (in contrast with temperature and pressure) does not allow an immediate calculation of heat capacity, even if the relation between E , S , and V is known. For C_V the situation is immediately correctable, because at fixed volume, $d\mathcal{W} = -PdV = 0$ and hence, according to Eq. (18), $dQ = dE$. Hence we may write

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V. \quad (1.24)$$

²⁴ A similar duality is possible for other pairs $\{q_j, \mathcal{F}_j\}$ of generalized coordinates and forces as well. For example, if a long sample of a dielectric placed is into a parallel, uniform external electric field, value of field $\mathcal{E}$ is fixed, i.e. does not depend on sample’s polarization. However, if a thin sheet of such material is perpendicular to the field, then value of field D is fixed – see, e.g., EM Sec. 3.4.

²⁵ The same is true for work $\mathcal{W}$, and in some textbooks this fact is emphasized by using a special sign for differentials of these variables. I do not do this in my notes, because both $d\mathcal{W}$ and dQ are still very much usual differentials: for example, $d\mathcal{W}$ is the difference between the mechanical work which has been done over our system by the end of the infinitesimal interval we are considering, and that done by the beginning of that interval.

so that in order to calculate C_V from a certain statistical-physics model, we only need to calculate E as a function of temperature and volume.

If we want to write similarly a convenient expression for C_P , the best way is to introduce a new notion of so-called *thermodynamic potentials* - whose introduction and effective use is perhaps one of the most impressive formalisms of thermodynamics. For that, let us combine Eqs. (1) and (18) to write the “1st law of thermodynamics” in its most common form

$$dQ = dE + PdV. \quad (1.25)$$

At an isobaric process (Fig. 5), i.e. at $P = \text{const}$, this expression is equivalent to

$$(dQ)_P = dE + d(PV) = d(E + PV)_P. \quad (1.26)$$

Thus, if we introduce a new function with the dimensionality of energy:

$$H \equiv E + PV, \quad (1.27)$$

Enthalpy:
definition

called *enthalpy* (or, more rarely, the “heat function” or “heat contents”),²⁶ we may rewrite Eq. (23) as

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P. \quad (1.28)$$

Comparing Eq. (28) with (24) we see that for the heat capacity, enthalpy H plays the same role at fixed pressure as the internal energy E plays at fixed volume.

Now let us explore properties of the enthalpy for an arbitrary reversible process, i.e. lifting the restriction $P = \text{const}$, but still keeping definition (27). Differentiating it, we get

$$dH = dE + PdV + VdP, \quad (1.29)$$

so that plugging in Eq. (17) for dE , we see that two terms PdV cancel, yielding a very simple expression

$$dH = TdS + VdP. \quad (1.30)$$

Enthalpy:
differential

This equation shows that if H has been found (say, experimentally measured or calculated for a certain microscopic model) as a function of entropy S and pressure P , we can find temperature T and volume V by simple partial differentiation:

$$T = \left(\frac{\partial H}{\partial S} \right)_P, \quad V = \left(\frac{\partial H}{\partial P} \right)_S. \quad (1.31)$$

The comparison of the first of these relations with Eq. (9) shows that not only for the heat capacity, but for temperature as well, enthalpy plays the same role at fixed pressure as played by the intrinsic energy at fixed volume. Moreover, the comparison of the second of Eqs. (31) with Eq. (15) shows that the transfer between E to H corresponds to a simple swap of $(-P)$ and V in the expressions for the differentials of these variables.

This success immediately raises the question whether we could develop it further on, by defining other useful *thermodynamic potentials* – variables with the dimensionality of energy that would have

²⁶ This function (as well as the Gibbs free energy G , see below), had been introduced in 1875 by J. Gibbs, though the term “enthalpy” was coined much later by H. Onnes.

similar properties, first of all a potential which would enable a similar swap of T and S in its full differential. We already know that the adiabatic processes is the reversible process with fixed entropy, so that now we should analyze a reversible process with fixed temperature. Such *isothermal process* may be implemented, for example, by placing the system under consideration into a thermal contact with a much larger system (called either the *heat bath*, or “heat reservoir”, or “thermostat”) that remains in thermodynamic equilibrium at all times – see Fig. 5.

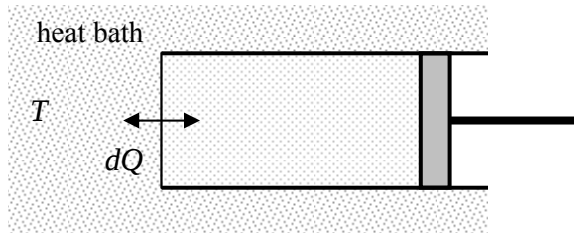


Fig. 1.5. The simplest implementation of an isothermal process.

Due to its large size, the heat bath temperature T does not depend on what is being done with our system, and if the change is being done slowly enough (i.e. reversibly), that temperature is also the temperature of our system – see Eq. (8) and its discussion. Let us calculate the elementary work $d\mathcal{W}$ for such a reversible isothermal process. According to the general Eq. (18), $d\mathcal{W} = dE - dQ$. Plugging in dQ from Eq. (19), for $T = \text{const}$ we get

$$(d\mathcal{W})_T = dE - TdS = d(E - TS) = dF, \quad (1.32)$$

where the following combination,

$$F \equiv E - TS, \quad (1.33)$$

is called the *free energy* (or the “Helmholtz free energy”, or just the “Helmholtz energy”²⁷). Just as we have done for the enthalpy, let us establish properties of this new thermodynamic potential for an arbitrary (not necessarily isothermal) small reversible variation of variables, while keeping definition (33). Differentiating this relation and using Eq. (17), we get

$$dF = -SdT - PdV. \quad (1.34)$$

Thus, if we know function $F(T, V)$, we can calculate S and P by simple differentiation:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad P = -\left(\frac{\partial F}{\partial V}\right)_T. \quad (1.35)$$

It is easy to see that we can make the derivative system full and symmetric if we introduce one more thermodynamic potential. Indeed, we have shown that each of three already introduced thermodynamic potentials (E , H , and F) has especially simple full differential if it is considered a

²⁷ After H. von Helmholtz (1821-1894). The last term was recommended by the most recent (1988) IUPAC’s decision, but I will use the first term, which prevails in physics literature. Its origin may stem from Eq. (32): F is may be interpreted as the internal energy part which is “free” to be transferred to mechanical work - at a reversible, isothermal process only!

function of two *canonical* arguments: one of “thermal variables” (either S or T) and one of “mechanical variables” (either P or V):²⁸

$$E = E(S, V), \quad H = H(S, P), \quad \text{and} \quad F = F(T, V). \quad (1.36)$$

In this list of pair of 4 arguments, only one pair is missing: (T, P) . The thermodynamic function of this pair, which gives two other variables (S and V) by simple differentiation, is called the *Gibbs energy* (or sometimes the “Gibbs free energy”): $G = G(T, P)$. The way to define it in a symmetric way is evident from the so-called *circular diagram* shown in Fig. 6.

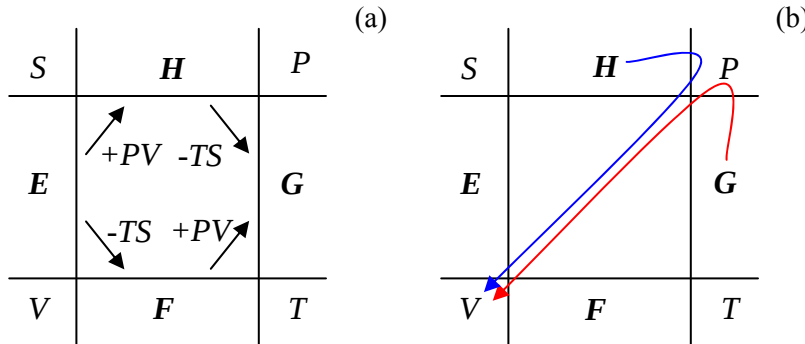


Fig. 1.6. (a) Circular diagram and (b) its use for variable calculation. The thermodynamic potentials are shown in boldface, each flanked by its two canonical arguments.

In this diagram, each thermodynamic potential is placed between its two canonical arguments – see Eq. (36). The left two arrows in Fig. 6a show the way the potentials H and F have been obtained from energy E – see Eqs. (27) and (33). This diagram hints that G has to be defined as shown by the right two arrows on that panel, i.e. as

$$G \equiv E - TS + PV = H - TS = F + PV. \quad (1.37)$$

Gibbs
energy:
definition

In order to verify this idea, let us calculate the full differential of this new potential, using, e.g., the last form of Eq. (37) together with Eq. (32):

$$dG = dF + d(PV) = (-SdT - PdV) + (PdV + VdP) = -SdT + VdP, \quad (1.38)$$

Gibbs
energy:
differential

so that if we know the function $G(T, P)$, we can indeed readily calculate entropy and volume:

$$S = -\left(\frac{\partial G}{\partial T}\right)_P, \quad V = \left(\frac{\partial G}{\partial P}\right)_T. \quad (1.39)$$

The circular diagram completed in this way is a good mnemonic tool for describing Eqs. (9), (15), (31), (35), and (39), which express thermodynamic variables as partial derivatives of the thermodynamic potentials. Indeed, the variable in any corner of the diagram may be found as a derivative of any of two potentials that are not its immediate neighbors, over the variable in the opposite corner. For example, the red line in Fig. 6b corresponds to the second of Eqs. (39), while the blue line, to the second of Eqs. (31). At this, the derivatives giving variables of the upper row (S and P) have to be

²⁸ Note the similarity of this situation with that in analytical (classical) mechanics (see, e.g., CM Chapters 2 and 10): the Lagrangian function may be used to get simple equations of motion if it is expressed as a function of generalized coordinates and *velocities*, while in order to use the Hamiltonian function in a similar way, it has to be expressed as a function of the generalized coordinates and *momenta*.

taken with negative signs, while those giving the variables of the bottom row (V and T), with positive signs.²⁹

Now I have to justify the collective name “thermodynamic potentials” used for E , H , F , and G . For that, let us consider an *irreversible* process, for example, a direct thermal contact of two bodies with different initial temperatures. As we have seen in Sec. 2, at such a process, the entropy may grow even without the external heat flow: $dS \geq 0$ at $dQ = 0$ – see Eq. (12). For a more general process with $dQ \neq 0$, this means that entropy may grow faster than predicted by Eq. (19), which has been derived for a reversible process, so that

$$dS \geq \frac{dQ}{T}, \quad (1.40)$$

with the equality approached in the reversible limit. Plugging Eq. (40) into Eq. (18) (which, being just the energy conservation law, remains valid for irreversible processes as well), we get

$$dE \leq TdS - PdV. \quad (1.41)$$

Now we can use this relation to have a look at the behavior of other thermodynamic potentials in irreversible situations, still keeping their definitions given by Eqs. (27), (33), and (37). Let us start from the (very common) case when both temperature T and volume V are kept constant. If the process was reversible, according to Eq. (34), the full time derivative of free energy F would equal zero. Equation (41) says that at the irreversible process it is not necessarily so: if $dT = dV = 0$, then

$$\frac{dF}{dt} = \frac{d}{dt}(E - TS) = \frac{dE}{dt} - T \frac{dS}{dt} \leq T \frac{dS}{dt} - T \frac{dS}{dt} = 0. \quad (1.42)$$

Hence, in the general (irreversible) situation, function F can only decrease, but not increase in time. This means that F eventually approaches its minimum value $F(T, S)$, which is given by the equations of reversible thermodynamics.

Thus in the case $T = \text{const}$, $V = \text{const}$, the free energy F , i.e. the difference $E - TS$, plays the role of the potential energy in the classical mechanics of dissipative processes: its minimum corresponds to the (in the case of F , thermodynamic) equilibrium of the system. This is one of the key results of thermodynamics, and I invite the reader to give it some thought. One of its possible handwaving interpretations is that the heat bath with fixed $T > 0$, i.e. with a substantial thermal agitation of its components, “wants” to impose thermal disorder in the system immersed in it by “rewarding” it (by lowering its F) for any increase of disorder.

Repeating the calculation for the case $T = \text{const}$, $P = \text{const}$, it is easy to see that in this case the same role is played by the Gibbs energy:

$$\frac{dG}{dt} = \frac{d}{dt}(E - TS + PV) = \frac{dE}{dt} - T \frac{dS}{dt} + P \frac{dV}{dt} \leq (T \frac{dS}{dt} - P \frac{dV}{dt}) - T \frac{dS}{dt} + P \frac{dV}{dt} = 0, \quad (1.43)$$

²⁹ There is also a wealth of other relations between thermodynamic variables that may be presented as second derivatives of the thermodynamic potentials, including four *Maxwell relations* such as $(\partial S/\partial V)_T = (\partial P/\partial T)_V$, etc. (They may be readily recovered from the well-known property of a function of two independent arguments, say, $f(x, y)$: $\partial(\partial f/\partial x)/\partial y = \partial(\partial f/\partial y)/\partial x$.) In this chapter, I will list only the thermodynamic relations that will be used later in the course; a more complete list may be found, e.g., in Sec. 16 of the textbook by L. Landau and E. Lifshitz, *Statistical Physics, Part 1*, 3rd ed., Pergamon, 1980 (and later its re-printings).

so that the thermal equilibrium now corresponds to the minimum of G rather than F . One can argue very convincingly that the difference, $G - F = PV$ between these two potentials (also equal to $H - E$) has very little to do with thermodynamics at all, because this difference exists (although not much advertised) in classical mechanics as well.³⁰ Indeed, the difference may be generalized as $G - F = -\mathcal{F}q_j$, where q_j is any generalized coordinate and $\mathcal{F}$ is the corresponding generalized force - see Eq. (1) and its discussion. In this case the minimum of F corresponds to the equilibrium of an autonomous system (with $\mathcal{F} = 0$), while the equilibrium position of the same system under the action of external force $\mathcal{F}$ is given by the minimum of G . Thus the external force “wants” the system to subdue to its effect, “rewarding” it by lowering its G . (The analogy with the “disorder pressure” by a heat bath, discussed in the last paragraph, is evident.)

For two remaining thermodynamic potentials, E and H , the calculations similar to Eqs. (42) and (43) make less sense, because that would require taking $S = \text{const}$ (with $V = \text{const}$ for E , and $P = \text{const}$ for H), but it is hard to prevent the entropy from growing if initially it had been lower than its equilibrium value, at least on the long-term basis.³¹ Thus the circular diagram is not so symmetric after all: G and/or F are somewhat more useful for most practical calculations than E and H .

One more important conceptual question is why the main task of statistical physics should be the calculation of thermodynamic potentials, rather than just a relation between P , V , and T . (Such relation is called the *equation of state* of the system.) Let us explore this issue on the example of an *ideal classical gas* in thermodynamic equilibrium, for which the equation of state should be well known to the reader from undergraduate physics (in Chapter 3, we will be derived from statistics):

$$PV = NT, \quad (1.44)$$

Ideal gas:
equation
of state

where N is the number of particles in volume V .³² Let us try to use it for the calculation of all thermodynamic potentials, and all other thermodynamic variables discussed above. We may start, for example, from the calculation of the free energy F . Indeed, solving Eq. (44) for pressure, $P = NT/V$, and integrating the second of Eqs. (35), we get

$$F = -\int P dV|_T = -NT \int \frac{dV}{V} = -NT \int \frac{d(V/N)}{(V/N)} = -NT \ln \frac{V}{N} + Nf(T), \quad (1.45)$$

where I have divided V by N in both instances just to present F as a manifestly extensive variable, in this uniform system proportional to N . The integration “constant” $f(T)$ is some function of temperature that cannot be recovered from the equation of state. This function also affects all other thermodynamic potentials, and entropy. Indeed, using the first of Eqs. (35) together with Eq. (45), we get

³⁰ See, e.g., CM Sec. 1.5.

³¹ There are a few practical systems, notably including the so-called *magnetic refrigerators* (to be discussed in Chapter 4), when the natural growth of S is so slow that the condition $S = \text{const}$ may be closely approached.

³² This equation was first derived from experimental data by E. Clapeyron (in 1834) in the form $PV = nRT_K$, where n is the number of moles in the gas sample, and $R \approx 8.31 \text{ J/mole}\cdot\text{K}$ is the so-called *gas constant*. This form is equivalent to Eq. (44), taking into account that $R = k_B N_A$, where $N_A \approx 6.02 \times 10^{23} \text{ mole}^{-1}$ is the so-called *Avogadro number*, i.e. the number of molecules per mole. (By definition of the mole, N_A is just the reciprocal mass, in grams, of a baryon - more exactly, by convention, of a $1/12^{\text{th}}$ part of the carbon-12 atom.)

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = N \left[\ln \frac{V}{N} - \frac{df}{dT} \right], \quad (1.46)$$

and now can combine Eqs. (33) and (46) to calculate the (internal) energy,

$$E = F + TS = \left(-NT \ln \frac{V}{N} + Nf \right) + T \left(N \ln \frac{V}{N} - N \frac{df}{dT} \right) = N \left(f - T \frac{df}{dT} \right), \quad (1.47)$$

then use Eqs. (27), (44) and (47) to calculate enthalpy,

$$H = E + PV = E + NT = N \left(f - T \frac{df}{dT} + T \right), \quad (1.48)$$

and, finally, plug Eqs. (44), and (45) into Eq. (37) to calculate the Gibbs energy

$$G = F + PV = N \left(-T \ln \frac{V}{N} + f + T \right). \quad (1.49)$$

In particular, Eq. (47) describes a very important property of the ideal classical gas: its energy depends only on temperature, but not on volume or pressure. One might question whether function $f(T)$ may be physically insignificant, just like the arbitrary constant that may be always added to the potential energy in nonrelativistic mechanics. In order to address this concern, let us calculate, from Eqs. (24) and (28), both heat capacities, that are readily measurable quantities:

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = -NT \frac{d^2 f}{dT^2}, \quad (1.50)$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = N \left(-T \frac{d^2 f}{dT^2} + 1 \right) = C_V + N. \quad (1.51)$$

We see that function $f(T)$, or at least its second derivative, is measurable.³³ (In Chapter 3, we will calculate this function for two simple “microscopic” models of the ideal classical gas.) The meaning of this function is evident from the physical picture of the ideal gas: pressure P exerted on the walls of the containing volume is produced only by the translational motion of the gas molecules, while their internal energy E (and hence other thermodynamic potentials) may be also contributed by the internal motion of the molecules – their rotations, vibrations, etc. Thus, the equation of state does *not* give the full thermodynamic description of a system, while the thermodynamic potentials do.

1.5. Systems with variable number of particles

Now we have to consider one more important case when the number N of particles in a system is not rigidly fixed, but may change as a result of a thermodynamic process. Typical examples of such a system is a gas sample separated from the environment by a penetrable partition (Fig. 7), and a gas in a contact with the liquid of the same molecules.

³³ Note, however, that the difference $C_P - C_V = N$ (if temperature is measured in kelvins, $C_P - C_V = nR$) is independent of $f(T)$. (It is possible to show that the difference $C_P - C_V$ is fully determined by the equation of state for *any* medium.)

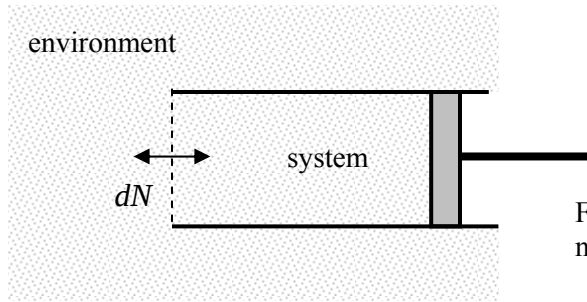


Fig. 1.7. Example of a system with variable number of particles.

Let us analyze this situation for the simplest case when all the particles are similar (though the analysis may be readily extended to systems with particle of several sorts). In this case we can consider N as an independent thermodynamic variable whose variation may change energy E of the system, so that (for a slow, reversible process) Eq. (17) should be now generalized as

$$dE = TdS - PdV + \mu dN, \quad (1.52)$$

Chemical potential: definition

where μ is a new function of state, called the *chemical potential*.³⁴ Keeping the definitions of other thermodynamic potentials, given by Eqs. (27), (33), and (37) intact, we see that expressions for their differentials should be generalized as

$$dH = TdS + VdP + \mu dN, \quad (1.53a)$$

$$dF = -SdT - PdV + \mu dN, \quad (1.53b)$$

$$dG = -SdT + VdP + \mu dN, \quad (1.53c)$$

so that the chemical potential may be calculated as either of the following derivatives:³⁵

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{S,V} = \left(\frac{\partial H}{\partial N} \right)_{S,P} = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \left(\frac{\partial G}{\partial N} \right)_{T,P}. \quad (1.54)$$

Despite their similarity, one of Eqs. (53)-(54) is more consequential than the others. Indeed, the Gibbs energy G is the only thermodynamic potential that is a function of two *intensive* parameters, T and P . However, as all thermodynamic potentials, G has to be extensive, so that in a system of similar particles it has to be proportional to N :

$$G = Nf(T, P). \quad (1.55)$$

Plugging this expression into the last of Eqs. (54), we see that μ equals $f(T, P)$. In other words,

$$\mu = \frac{G}{N}, \quad (1.56)$$

Chemical potential as the Gibbs energy

so that the chemical potential is just *the Gibbs energy per particle*.

³⁴ This name, of a historic origin, is a bit misleading: as evident from Eq. (52), μ has a clear *physical* sense of the average energy cost of adding one more particle to the system of $N \gg 1$ particles.

³⁵ Note that strictly speaking, Eqs. (9), (15), (31), (35) and (39) should be now generalized by adding one more lower index, N , to the corresponding derivatives.

In order to demonstrate how vital the notion of chemical potential may be, let us consider the situation (parallel to that shown in Fig. 2) when a system consists of two parts, with equal pressure and temperature, that can exchange particles at a relatively slow rate (much slower than the speed of internal relaxation inside each of the parts). Then we can write two equations similar to Eq. (5):

$$N = N_1 + N_2, \quad G = G_1 + G_2, \quad (1.57)$$

where $N = \text{const}$, and Eq. (56) may be used to describe each component of G :

$$G = \mu_1 N_1 + \mu_2 N_2. \quad (1.58)$$

Plugging N_2 expressed from the first of Eqs. (57), $N_2 = N - N_1$, into Eq. (58), we see that

$$\frac{dG}{dN_1} = \mu_1 - \mu_2, \quad (1.59)$$

so that the minimum of G is achieved at $\mu_1 = \mu_2$. Hence, in the conditions of fixed temperature and pressure, i.e. when G is the appropriate thermodynamic potential, the chemical potentials of the system parts should be equal - the so-called *chemical equilibrium*.

Later we will also run into cases when volume V of a system, its temperature T , and the chemical potential μ are all fixed. (The last condition may be readily implemented by allowing the system of interest to exchange particles with a reservoir so large that its μ stays constant.) A thermodynamic potential appropriate for this case may be obtained from the free energy F by subtraction of the product μN , resulting is the so-called *grand thermodynamic potential* (or the “Landau potential”)

$$\Omega \equiv F - \mu N = F - \frac{G}{N} N = F - G = -PV. \quad (1.60)$$

Grand
potential:
definition
and full
differential

Indeed, for a reversible process, the full differential of this potential is

$$d\Omega = dF - d(\mu N) = (-SdT - PdV + \mu dN) - (\mu dN + Nd\mu) = -SdT - PdV - Nd\mu, \quad (1.61)$$

so that if Ω has been calculated as a function of T , V and μ , other thermodynamic variables may be found as

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V, \mu}, \quad P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T, \mu}, \quad N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V}. \quad (1.62)$$

For an irreversible process, acting exactly as we have done with other potentials, it is straightforward to prove that in the conditions of fixed T , V , and μ , $d\Omega/dt \leq 0$, so that system's equilibrium indeed corresponds to the minimum of the grand potential Ω .

1.6. Thermal machines

In order to complete this brief review of thermodynamics, I cannot pass the topic of *thermal machines* – not because it will be used much in this course, but mostly because of its practical and historic significance. (Indeed, the whole field of thermodynamics was spurred by the famous 1824 work by S. Carnot, which in particular gave an alternative, indirect form of the 2nd law of thermodynamics – see below.)

Figure 8a shows the generic scheme of a thermal machine that may perform mechanical work on the environment (in the notation of Eq. (1), equal to $-\mathcal{W}$) during each cycle of the expansion/compression of the “working gas”, by transferring different amounts of heat from a high-temperature heat bath (Q_H) and to the low-temperature bath (Q_L). One relation between three amounts Q_H , Q_L , and $\mathcal{W}$ is immediately given by the energy conservation (i.e. by “the 1st law of thermodynamics”):

$$Q_H - Q_L = -\mathcal{W}. \quad (1.63)$$

From Eq. (1), the mechanical work during the cycle may be calculated as

$$-\mathcal{W} = \oint P dV, \quad (1.64)$$

i.e. equals the area circumvented by the representing point on the $[P, V]$ plane – see Fig. 8b.³⁶ Hence, the work depends on the exact form of the cycle, which in turn depends not only on T_H and T_L , but also on working gas’ properties.

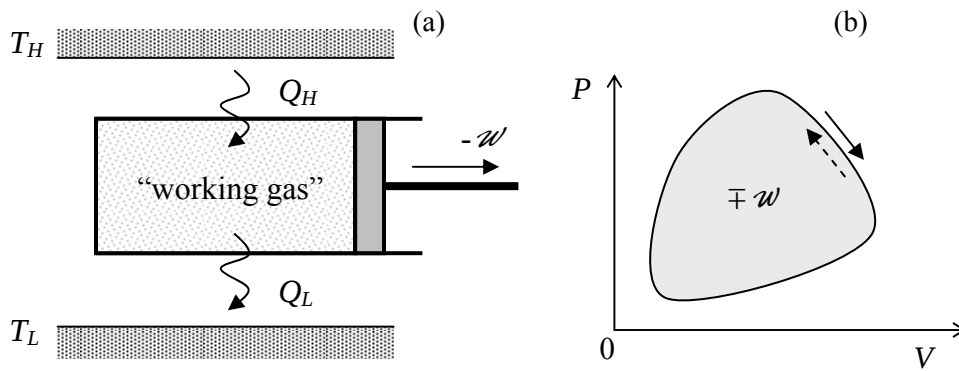


Fig. 1.8. (a) The simplest implementation of a thermal machine, and (b) the graphic presentation of the mechanical work it performs. On panel (b), solid arrow indicates the heat engine cycle direction, while the dashed arrow, the refrigerator cycle direction.

An exception from this rule is the famous *Carnot cycle*, consisting of two isothermal and two adiabatic processes (all reversible!). In its heat engine’s form, the cycle starts from an isothermic expansion of the gas in contact with the hot bath (i.e. at $T = T_H$), followed by its additional adiabatic expansion until T drops to T_L . Then an isothermal compression of the gas is performed in its contact with the cold bath (at $T = T_L$), followed by its additional adiabatic compression to raise its temperature to T_H again, after which the cycle is repeated again and again. (Note that during this cycle the working gas is never in contact with both heat baths simultaneously, thus avoiding the irreversible heat transfer between them.) The cycle’s shape on the $[V, P]$ plane depends on exact properties of the working gas and may be rather complicated. However, since the entropy is constant at any adiabatic process, the Carnot cycle shape on the $[S, T]$ plane is always rectangular – see Fig. 9.³⁷

³⁶ Note that positive sign of the circular integral corresponds to the clockwise rotation of the point, so that work ($-\mathcal{W}$) done by the working gas is positive at the clockwise rotation (pertinent to *heat engines*) and negative in the opposite case (implemented in *refrigerators* and *heat pumps*).

³⁷ A cycle with an $[S, T]$ shape very close to the Carnot (rectangular) one may be implemented at the already mentioned magnetic (or “adiabatic-demagnetization”) refrigeration, using the alignment of either atomic or

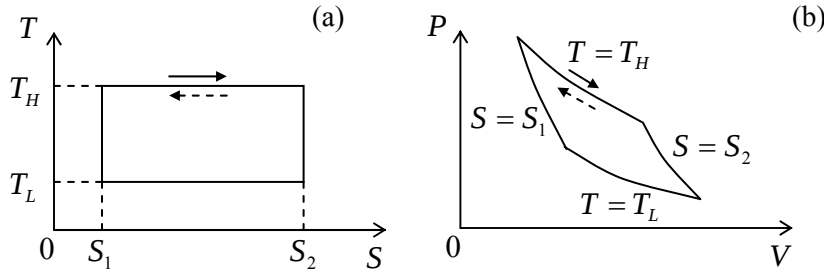


Fig. 1.9. Representation of the Carnot cycle (a) on the $[S, T]$ plane and (b) the $[V, P]$ plane (schematically). The meaning of arrows is the same as in Fig. 8.

Since during each isotherm, the working gas is brought into thermal contact only with the corresponding heat bath, Eq. (19), $dQ = TdS$ may be immediately integrated to yield

$$Q_H = T_H(S_2 - S_1), \quad Q_L = T_L(S_2 - S_1). \quad (1.65)$$

Hence the ratio of these two heat flows is completely determined by their temperature ratio:

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L}, \quad (1.66)$$

regardless of the working gas properties. Equations (63) and (66) are sufficient to find the ratio of work $-\mathcal{W}$ to any of Q_H and Q_L . For example, the main figure-of-merit of a thermal machine used as a heat engine ($Q_H > 0$, $Q_L > 0$, $-\mathcal{W} = |\mathcal{W}| > 0$), is its *efficiency*

Heat
engine
efficiency:
definition

$$\eta \equiv \frac{|\mathcal{W}|}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \leq 1. \quad (1.67)$$

For the Carnot cycle, Eq. (66) immediately yields the famous relation,

Carnot
cycle's
efficiency

$$\eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H}, \quad (1.68)$$

which shows that at given T_L (that is typically the ambient temperature ~ 300 K), the efficiency may be increased, ultimately to 1, by raising temperature of the heat source.

On the other hand, if the cycle is reversed (see the dashed arrows in Figs. 8 and 9), the same thermal machine may serve as a *refrigerator*, providing the heat removal from the low-temperature bath ($Q_L < 0$) for the cost of consuming external work: $\mathcal{W} > 0$. This reversal does not affect the basic relation (63) that may be used to calculate the relevant figure-of-merit, called the *cooling coefficient of performance* ($\text{COP}_{\text{cooling}}$)

$$\text{COP}_{\text{cooling}} \equiv \frac{|Q_L|}{\mathcal{W}} = \frac{Q_L}{Q_H - Q_L}. \quad (1.69)$$

Notice that this coefficient may readily be above unity; in particular, for the Carnot cycle we may use Eq. (66) (which is also unaffected by the cycle reversal) to get

nuclear spins by external magnetic field. In such refrigerators (to be further discussed in the next chapter), the role of the $\{-P, V\}$ pair of variables is played by the $\{\mathcal{H}, B\}$ pair – see Eq. (3).

$$(\text{COP}_{\text{cooling}})_{\text{Carnot}} = \frac{T_L}{T_H - T_L}, \quad (1.70)$$

so that the $\text{COP}_{\text{cooling}}$ is larger than 1 at $T_H < 2T_L$, and even may be very large when the temperature difference $(T_H - T_L)$, sustained by the refrigerator, tends to zero. For example, in a typical air-conditioning system, $T_H - T_L \sim T_L/30$, so that the Carnot value of $\text{COP}_{\text{cooling}}$ is as high as ~ 30 , while in the state-of-the-art commercial HVAC systems it is the range for 3 to 4. This is why the term “cooling efficiency”, used in some textbooks instead of $(\text{COP})_{\text{cooling}}$, may be misleading.

Since in the reversed cycle $Q_H = -\mathcal{W} + Q_L < 0$, the system also provides heat flow into the hotter heat bath, and thus may be used as a *heat pump*. However, the figure-of-merit appropriate for this application is different:

$$\text{COP}_{\text{heating}} \equiv \frac{|Q_H|}{\mathcal{W}} = \frac{Q_H}{Q_H - Q_L}, \quad (1.71)$$

so that for the Carnot cycle

$$(\text{COP}_{\text{heating}})_{\text{Carnot}} = \frac{T_H}{T_H - T_L}. \quad (1.72)$$

Note that this COP is *always* larger than 1, meaning that the Carnot heat pump is always more efficient than the direct conversion of work into heat (where $Q_H = -\mathcal{W}$, and $\text{COP}_{\text{heating}} = 1$), though practical electricity-driven heat pumps are substantially more complex (and hence more expensive) than, say, simple electric heaters. Such heat pumps, with typical $\text{COP}_{\text{heating}}$ values around 4 in summer and 2 in winter, are frequently used for heating large buildings.

I have dwelled so long on the Carnot cycle, because it has a remarkable property: the highest possible efficiency of all heat-engine cycles. Indeed, in the Carnot cycle the transfer of heat between any heat bath and the working gas is performed reversibly, when their temperatures are equal. If this is not so, heat might flow from a hotter to colder system without performing any work. Hence the result (68) also yields the maximum efficiency of *any* heat engine. In particular, it shows that $\eta_{\text{max}} = 0$ at $T_H = T_L$, i.e., no heat engine can perform any mechanical work in the absence of temperature gradients.³⁸ In some alternative axiomatic systems of thermodynamics, this fact, i.e. the impossibility of the direct conversion of heat to work, is postulated, and serves the role of the 2nd law.

Note also that according to Eq. (71), $\text{COP}_{\text{cooling}}$ of the Carnot cycle tends to zero at $T_L \rightarrow 0$, making it impossible to reach the absolute zero of temperature, and hence illustrating the meaningful (Nernst’s) formulation of the 3rd law of thermodynamics. Indeed, let us prescribe a certain (but very large) heat capacity $C(T)$ to the low-temperature bath, and use the definition of this variable to write the following evident expression for the (very small) change of its temperature as a result of a relatively number dn of similar refrigeration cycles:

$$C(T_L)dT_L = Q_L dn. \quad (1.73)$$

³⁸ Such a hypothetical (and impossible!) heat engine, which would violate the 2nd law of thermodynamics, is called the “perpetual motion machine of the 2nd kind” - in contrast to the “perpetual motion machine of the 1st kind” which would violate the 1st law, i.e., the energy conservation.

Together with Eq. (66), this relation yields

$$C(T_L)dT_L = -\frac{|Q_H|}{T_H}T_L dn, \quad (1.74)$$

so that if we perform many (n) cycles (with constant Q_H and T_H), the initial and final values of T_L obey the following equation

$$\int_{T_{\text{ini}}}^{T_{\text{fin}}} \frac{C(T)dT}{T} = -\frac{|Q_H|}{T_H}n. \quad (1.75)$$

For example, if $C(T)$ is a constant, Eq. (75) yields an exponential law,

$$T_{\text{fin}} = T_{\text{ini}} \exp\left\{-\frac{|Q_H|}{CT_H}n\right\}, \quad (1.76)$$

with the absolute zero not reached as any finite n . Relation (75) proves the Nernst theorem if $C(T)$ does not vanish at $T \rightarrow 0$, but for such metastable systems as glasses the situation is more complicated.³⁹ Fortunately, this issue does not affect other aspects of statistical physics – at least those to be discussed in this course.

1.7. Exercise problems

1.1. Two bodies, with negligible thermal expansion coefficients and constant heat capacities C_1 and C_2 , are placed into a weak thermal contact, at different initial temperatures T_1 and T_2 . Calculate the full change of entropy of the system before it reaches the full thermal equilibrium.

1.2. A gas has the following properties:

- (i) $C_V = aT^b$, and
- (ii) the work $\mathcal{W}_T$ needed for its isothermal compression from V_2 to V_1 equals $cT\ln(V_2/V_1)$,

where a , b , and c are constants. Find the equation of state of the gas, and calculate the temperature dependences of its entropy S , and thermodynamic potentials E , H , F , G and Ω .

1.3. A vessel with an ideal classical gas of indistinguishable molecules is separated by a partition so that the number N of molecules in both parts is the same but their volumes are different. The gas is in thermal equilibrium, and its pressure in one part is P_1 , and in another, P_2 . Calculate the change of entropy caused by a fast removal of the partition. Analyze the result.

1.4. An ideal classical gas of N particles, is initially confined to volume V , and let alone to reach the thermal equilibrium with a heat bath of temperature T . Then the gas is allowed to expand to volume $V' > V$ in one the following ways:

³⁹ For a detailed discussion of this issue see, e.g., J. Wilks, *The Third Law of Thermodynamics*, Oxford U. Press, 1961.

(i) The expansion slow, so that due to the thermal contact with the heat bath, the gas temperature remains equal to T all the time.

(ii) The partition separating volumes V and $(V' - V)$ is removed very fast, allowing the gas to expand rapidly.

For each process, calculate the changes of pressure, temperature, energy, and entropy of the gas during its expansion.

1.5. For an ideal classical gas with temperature-independent specific heat, derive the relation between P and V at the adiabatic expansion/compression.

1.6. Calculate the speed and wave impedance of acoustic waves in an ideal classical gas with temperature-independent C_P and C_V , in the limits when that the wave propagation may be treated as:

- (i) an isothermal process,
- (ii) an adiabatic process.

Which of these limits corresponds to higher wave frequencies?

1.7. As will be discussed in Sec. 3.5, the so-called “hardball” models of classical particle interaction yield the following equation of state of a gas of such particles:

$$P = T\varphi(n),$$

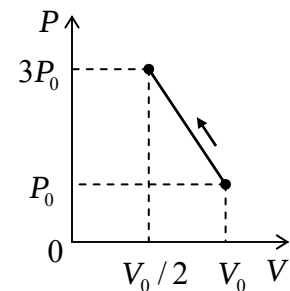
where $n = N/V$ is the particle density, and function $\varphi(n)$ is generally different from that ($\varphi_{\text{ideal}}(n) = n$) of the ideal gas. For such a gas, with temperature-independent C_V , calculate:

- (i) the energy of the gas, and
- (ii) its pressure as a function of n at adiabatic compression.

1.8. For an arbitrary thermodynamic system with a fixed number of particles, prove the following *Maxwell relations* (already mentioned in Sec. 1.4):

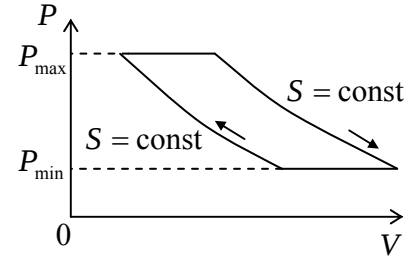
$$(i): \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \quad (ii): \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S, \quad (iii): \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \quad (iv): \left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S.$$

1.9. A process, performed with a fixed portion of an ideal gas, may be represented with a straight line on the $[P, V]$ plane – see Fig. on the right. Find the point at which the heat flow into/out of the gas changes its direction.

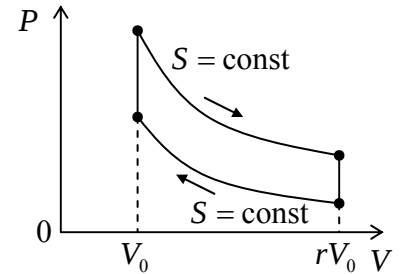


1.10. Two bodies have equal and constant heat capacities C , but different temperatures, T_1 and T_2 . Calculate the maximum mechanical work obtainable from this system, using a heat engine.

1.11. Express the efficiency of a heat engine that uses the “Joule cycle” consisting of two adiabatic and two isobaric processes (see Fig. on the right), via the minimum and maximum values of pressure, and compare the result with that for the Carnot cycle. Assume an ideal classical working gas with constant C_P and C_V .



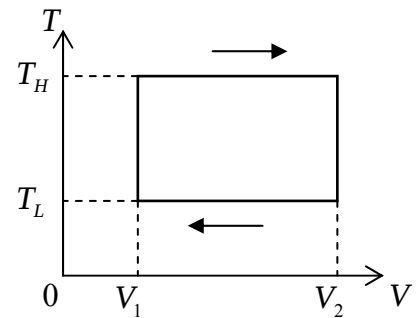
1.12. Calculate the efficiency of a heat engine using the “Otto cycle”,⁴⁰ which consists of two adiabatic and two isochoric (constant-volume) processes – see Fig. on the right. Explore how does the efficiency depend on the ratio $r \equiv V_{\max}/V_{\min}$, and compare it with Carnot cycle’s efficiency. Assume an ideal working gas with temperature-independent specific heat.



1.13. A heat engine’s cycle consists of two isothermal ($T = \text{const}$) and two isochoric ($V = \text{const}$) reversible processes - see Fig. on the right.

(i) Assuming that the working gas is an ideal classical gas of N particles, calculate the mechanical work performed by the engine during one cycle.

(ii) Are the specified conditions sufficient to calculate engine’s efficiency?



⁴⁰ This name stems from the fact that the cycle is an approximate model of operation of the four-stroke internal-combustion engine, which was improved and made practicable (though not invented!) by N. Otto in 1876.

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Chapter 2. Principles of Physical Statistics

This chapter is the key part of this course. It is started with a brief discussion of such basic notions of statistical physics as statistical ensembles, probability, and ergodicity. Then the so-called microcanonical distribution postulate is formulated in parallel with the statistical definition of entropy. The next step is the derivation of the Gibbs distribution, which is frequently considered the summit of the statistical physics, and one more, grand canonical distribution, which is more convenient for some tasks - in particular for the derivation of the Boltzmann, Fermi-Dirac, and Bose-Einstein statistics for systems of independent particles.

2.1. Statistical ensembles and probability

As has been already discussed in Sec. 1.1, statistical physics deals with systems in conditions when either the unknown initial conditions, or the system complexity, or the laws of motion (as in the case of quantum mechanics) do not allow a definite prediction of measurement results. The main formalism for the analysis of such systems is the probability theory, so let me start with a very brief review of its basic concepts using informal “physical” language - less rigorous but (hopefully) more transparent than a standard mathematical treatment.¹

Consider $N \gg 1$ independent similar experiments carried out with *apparently* similar systems (i.e. systems with identical *macroscopic* parameters such as volume, pressure, etc.), but still giving, by any of the reasons outlined above, different results of measurements. Such a collection of experiments, together with the fixed method of result processing, is a good example of a *statistical ensemble*. Let us start from the case when the experiments may have M different *discrete* outcomes, and the number of experiments giving the corresponding different results is $N_1, N_2, \dots, N_M$, so that

$$\sum_{m=1}^M N_m = N. \quad (2.1)$$

The *probability* of each outcome, for the given statistical ensemble, is then defined as

Probability

$$W_m \equiv \lim_{N \rightarrow \infty} \frac{N_m}{N}. \quad (2.2)$$

Though this definition is so close to our everyday experience that it is almost self-evident, a few remarks may still be relevant.

First, probabilities W_m depend on the exact statistical ensemble they are defined for, notably including the method of result processing. As an example, consider the standard coin tossing. For the ensemble of *all* tossed coins, the probabilities of both the heads and tails outcomes equal $\frac{1}{2}$. However, nothing prevents us from defining another statistical ensemble as a set of coin-tossing experiments with the heads-up outcome. Evidently, the probability of finding coins with tails up in this new ensemble is not $\frac{1}{2}$ but 0. Still, this set of experiments is not only legitimate but also a rather meaningful statistical

¹ For the reader interested in reviewing a more rigorous approach, I can recommend, for example, Chapter 18 of the handbook by G. Korn and T. Korn – see MA Sec. 16(ii).

ensemble; for example, the exact position and orientation of the tossed coins on the floor, within this restricted ensemble, may be rather random.

Second, a statistical ensemble does not necessarily require N different physical systems, e.g., N different coins. It is intuitively clear that tossing the same coin N times constitutes an ensemble with similar statistical properties. More generally, a set of N experiments with the same system provides a statistical ensemble equivalent to the set of experiments with N different systems, provided that the experiments are kept independent, i.e. that outcomes of past experiments do not affect those of the experiments to follow. Moreover, for most physical systems of interest any special preparation is unnecessary, and N different experiments, separated by sufficiently long time intervals, form a “good” statistical ensemble – the property called *ergodicity*.²

Third, the reference to infinite N in Eq. (2) does not strip the notion of probability from its practical relevance. Indeed, it is easy to prove (see Chapter 5) that, at very general conditions, at finite but sufficiently large N , numbers N_m are approaching their *average* (or *expectation*) *values*³

$$\langle N_m \rangle \equiv W_m N, \quad (2.3)$$

with the relative deviation scale decreasing as $1/\langle N_m \rangle^{1/2}$.

Now let me list those properties of probabilities that we will immediately need. First, dividing Eq. (1) by N and following the limit $N \rightarrow \infty$, we get the well-known *normalization condition*

$$\sum_{m=1}^M W_m = 1; \quad (2.4)$$

just remember that it is true only if each experiment definitely yields one of outcomes $N_1, N_2, \dots, N_M$. Next, if we have an additive function of results,

$$f = \frac{1}{N} \sum_{m=1}^M N_m f_m, \quad (2.5)$$

where f_m are some definite (deterministic) coefficients, we may define the *statistical average* (also called the *expectation value*) of the function as

$$\langle f \rangle \equiv \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{m=1}^M \langle N_m \rangle f_m, \quad (2.6)$$

² The most popular counter-example of a non-ergodic system is an energy-conserving system of particles placed in a potential which is a quadratic form of particle coordinates. Theory of oscillations tells us (see, e.g., CM Sec. 5.2) that this system is equivalent to a set of non-interacting harmonic oscillators. Each of these oscillators conserves its own initial energy E_j forever, so that the statistics of N measurements of one such system may differ from that of N different systems with random distribution of E_j , even if the total energy of the system, $E = \sum_j E_j$, is the same. Such non-ergodicity, however, is a rather feeble phenomenon, and is readily destroyed by any of “mixing” mechanisms, such as weak interaction with environment (leading, in particular, to oscillation damping), nonlinear interaction of the components (see, e.g., CM Ch. 4), and chaos (CM Ch. 9), all of them strongly enhanced by increasing the number of particles in the system, i.e. the number of its degrees of freedom. This is why most real-life systems are ergodic; for those interested in non-ergodic exotics, I can recommend the monograph by V. Arnold and A. Avez, *Ergodic Problems of Classical Mechanics*, Addison-Wesley, 1989.

³ Here, and everywhere in these notes, angle brackets $\langle \dots \rangle$ mean averaging over a statistical ensemble, which is generally different from averaging over time – as it will be the case in quite a few examples considered below.

so that using Eq. (3) we get

Expectation
value via
probabilities

$$\langle f \rangle = \sum_{m=1}^M W_m f_m. \quad (2.7)$$

Notice that Eq. (3) may be considered as the particular form of this general result, for all $f_m = 1$.

Next, the spectrum of possible experimental outcomes is frequently continuous. (Think, for example, about the positions of the marks left by bullets fired into a target from a far.) The above formulas may be readily generalized to this case; let us start from the simplest situation when all different outcomes may be described by one continuous variable q , which replaces the discrete index m in Eqs. (1)-(7). The basic relation for this case is the self-evident fact that the probability dW of having an outcome within a very small interval dq near point q is proportional to the magnitude of that interval:

$$dW = w(q)dq. \quad (2.8)$$

Function $w(q)$, which does not depend on dq , is called the *probability density*. Now all the above formulas may be recast by replacing probabilities W_m by products (8), and the summation over m , by integration over q . In particular, instead of Eq. (4) the normalization condition now becomes

$$\int w(q)dq = 1, \quad (2.9)$$

where the integration should be extended over the whole range of possible values of q . Similarly, instead by Eq. (5), it is natural to consider a function $f(q)$. Then instead of Eq. (7), the expectation value of the function may be calculated as

Expectation
value via
probability
distribution

$$\langle f \rangle = \int w(q)f(q)dq. \quad (2.10)$$

It is straightforward to generalize these formulas to the case of more variables. For example, results of measurements of a particle with 3 degrees of freedom may be described by the probability density w defined in the 6D space of its generalized radius-vector $\mathbf{q}$ and momentum $\mathbf{p}$. As a result, the expectation value of a function of these variables may be expressed as a 6D integral

$$\langle f \rangle = \int w(\mathbf{q}, \mathbf{p})f(\mathbf{q}, \mathbf{p})d^3q d^3p. \quad (2.11)$$

Some systems considered in this course consist of components whose quantum properties cannot be ignored, so let us discuss how $\langle f \rangle$ should be calculated in this case. If by f_m we mean measurement results, Eq. (7) (and its generalizations) of course remains valid, but since these numbers themselves may be affected by the intrinsic quantum-mechanical uncertainty, it may make sense to have a bit deeper look into this situation. Quantum mechanics tells us⁴ that the most general expression for the expectation value of an observable f in a certain ensemble of macroscopically similar systems is

$$\langle f \rangle = \sum_{m, m'} W_{mm'} f_{m'm} \equiv \text{Tr}(Wf). \quad (2.12)$$

Here $f_{mm'}$ are the matrix elements of the quantum-mechanical operator $\hat{f}$ corresponding to the observable f , in a full basis of orthonormal states m ,

$$f_{mm'} = \langle m | \hat{f} | m' \rangle, \quad (2.13)$$

⁴ See, e.g., QM Sec. 6.1.

while coefficients $W_{mm'}$ are elements of the so-called *density matrix* W , which represents, in the same basis, a *density operator* $\hat{W}$ describing properties of this ensemble. Equation (12) is evidently more general than Eq. (7), and is reduced to it only if the density matrix is diagonal:

$$W_{mm'} = W_m \delta_{mm'}, \quad (2.14)$$

(where $\delta_{mm'}$ is the Kronecker symbol), when the diagonal elements W_m play the role of probabilities of the corresponding states.

Thus the largest difference between the quantum and classical description is the presence, in Eq. (12), of the off-diagonal elements of the density matrix. They have largest values in the *pure* (also called “coherent”) ensemble, in which the state of the system may be described with *state vectors*, e.g., the *ket-vector*

$$|\alpha\rangle = \sum_m \alpha_m |m\rangle, \quad (2.15)$$

where α_m are some complex coefficients. In this simple case, the density matrix elements are merely

$$W_{mm'} = \alpha_m^* \alpha_{m'}, \quad (2.16)$$

so that the off-diagonal elements are of the same order as the diagonal elements. For example, in the very important particular case of a *two-level system*, the pure-state density matrix is

$$W = \begin{pmatrix} \alpha_1^* \alpha_1 & \alpha_1^* \alpha_2 \\ \alpha_2^* \alpha_1 & \alpha_2^* \alpha_2 \end{pmatrix}, \quad (2.17)$$

so that the product of its off-diagonal components is as large as that of the diagonal components. In the most important basis of stationary states, i.e. eigenstates of system’s time-independent Hamiltonian, coefficients α_m oscillate in time as⁵

$$\alpha_m(t) = \alpha_m(0) \exp\left\{-i \frac{E_m}{\hbar} t\right\} = |\alpha_m| \exp\left\{-i \frac{E_m}{\hbar} t + i \varphi_m\right\}, \quad (2.18)$$

where E_m are the corresponding eigenenergies, and φ_m are constant phase shifts. This means that while the diagonal terms of the density matrix (16) remain constant, its off-diagonal components are oscillating functions of time:

$$W_{mm'} = \alpha_{m'}^* \alpha_m = |\alpha_{m'}| |\alpha_m| \exp\left\{i \frac{E_m - E_{m'}}{\hbar} t\right\} \exp\{i(\varphi_{m'} - \varphi_m)\}. \quad (2.19)$$

Due to the extreme smallness of the Planck constant (on the human scale of things), a miniscule random perturbations of eigenenergies are equivalent to substantial random changes of the phase multiplier, so that the time average of any off-diagonal matrix element tends to zero. Moreover, even if our statistical ensemble consists of systems with exactly the same E_m , but different values φ_m (which are typically hard to control at the initial preparation of the system), the average values of all $W_{mm'}$ (with $m \neq m'$) vanish again.

⁵ Here I use the Schrödinger picture of quantum mechanics in which the matrix elements f_{mn} do not evolve in time.

This is why, besides some very special cases, typical statistical ensembles of quantum particles are far from being pure, and in most cases (certainly including the thermodynamic equilibrium), a good approximation for their description is given by the opposite limit of the so-called *classical mixture* in which all off-diagonal matrix elements of the density matrix equal zero, and its diagonal elements W_{mm} are merely the probabilities W_m of the corresponding eigenstates. In this case, for observables compatible with energy, Eq. (12) is reduced to Eq. (7), with f_m being the eigenvalues of variable f .

2.2. Microcanonical ensemble and distribution

Let us start with the discussion of physical statistics with the simplest, *microcanonical statistical ensemble*⁶ that is defined a set of macroscopically similar closed (isolated) systems with *virtually* the same total energy E . Since in quantum mechanics the energy of a closed system is quantized, it is convenient to include into the ensemble all systems with energies E_m within a narrow interval $\Delta E \ll E$, that is nevertheless much larger than the average distance δE between the energy levels, so that the number M of different quantum states within interval ΔE is large, $M \gg 1$. Such choice of ΔE is only possible if $\delta E \ll E$; however, the reader should not worry too much about this condition, because the most important applications of the microcanonical ensemble are for very large systems (or very high energies) when the energy spectrum is very dense.⁷

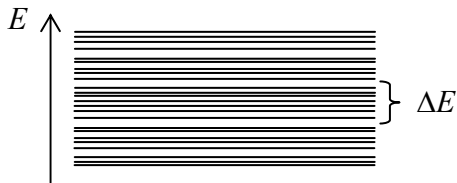


Fig. 2.1. *Very* schematic image of the microcanonical ensemble. (Actually, the ensemble deals with quantum states rather than energy levels. An energy level may be degenerate, i.e. correspond to several states.)

This ensemble serves as the basis for the formulation of a postulate which is most frequently called the *microcanonical distribution* (or sometimes the “main statistical hypothesis”): *in the thermodynamic equilibrium, all possible states of the microcanonical ensemble have equal probability*,

$$W_m = \frac{1}{M} = \text{const.} \quad (2.20)$$

Micro-
canonical
distribution

Though in some constructs of statistical mechanics this equality is derived from other axioms, which look more plausible to their authors, I believe that Eq. (20) may be taken as the starting point of the statistical physics, supported “just” by the compliance of all its corollaries with experimental observations.⁸

Note that postulate (20) sheds a light on the nature of the macroscopic irreversibility of microscopically reversible (closed) systems: if such a system was initially in a certain state, its time

⁶ The terms “microcanonical”, as well as “canonical” (see Sec. 4 below) are apparently due to J. Gibbs, and I could not find out his motivation for these names. (“Canonical” in the sense of “standard” or “common” is quite appropriate, but why “micro”?)

⁷ Formally, the main result of this section, Eq. (20), is valid for any M (including $M = 1$), it is just less informative for small M - and trivial for $M = 1$.

⁸ Though I have to move on, let me note that the microcanonical distribution (20) is a very nontrivial postulate, and my advice to the reader to give some thought to this foundation of the whole building of statistical mechanics.

evolution with just miniscule interactions with environment (which is necessary for reaching the thermodynamic equilibrium) would eventually lead to the uniform distribution of its probability among all states with the essentially same energy. Each of these states is not “better” than the initial one; rather, in a macroscopic system, there are just so many of these states that the chance to find the system in the initial state is practically nil - again, think about the ink drop diffusion into a glass of water.

Now let us find a suitable definition of entropy S of a microcanonical ensemble member - for now, in the thermodynamic equilibrium only. Since S is a measure of *disorder*, it should be related to the amount of information *lost* when the system goes from the full order to the full disorder, i.e. into the microcanonical distribution (20), or, in other words, the amount of information⁹ *necessary* to find the exact state of your system in a microcanonical ensemble.

In the information theory, the amount of information necessary to make a definite choice between two options with equal probabilities (Fig. 2a) is defined as

$$I(2) \equiv \log_2 2 = 1. \quad (2.21)$$

This unit of information is called a *bit*. Now, if we need to make a choice between 4 equally probable opportunities, it can be made in two similar steps (Fig. 2b), each requiring one bit of information, so that the total amount of information necessary for the choice is

$$I(4) = 2I(2) = 2 = \log_2 4. \quad (2.22)$$

An obvious extension of this process to the choice between $M = 2^m$ states gives

$$I(M) = mI(2) = m = \log_2 M. \quad (2.23)$$

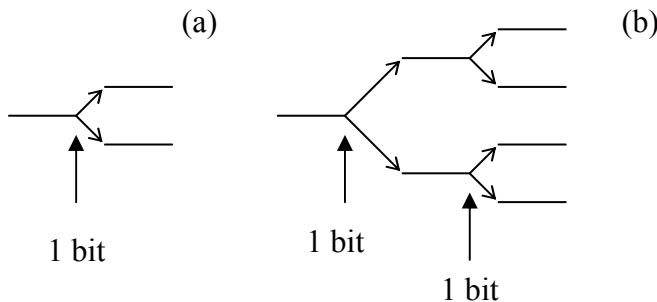


Fig. 2.2. “Logarithmic trees” of binary decisions for making a choice between (a) 2 and (b) 4 opportunities with equal probabilities.

This measure, if extended naturally to any integer M , is quite suitable for the definition of entropy at equilibrium, with the only difference that, following tradition, the binary logarithm is replaced with the natural one:¹⁰

⁹ I will rely on reader’s common sense and intuitive understanding what information is, because in the formal information theory this notion is also essentially postulated - see, e.g., the wonderfully clear text by J. Pierce, *An Introduction to Information Theory*, Dover, 1980.

¹⁰ This is of course just the change of a constant factor: $S(M) = \ln M = \ln 2 \times \log_2 M = \ln 2 \times I(M) \approx 0.693 I(M)$. A review of Chapter 1 shows that nothing in thermodynamics prevents us from choosing such coefficient arbitrarily, with the corresponding change of the temperature scale - see Eq. (1.9). In particular, in the SI units, Eq. (24b) becomes $S = -k_B \ln W_m$, so that one bit of information corresponds to the entropy change $\Delta S = k_B \ln 2 \approx 0.693 k_B \approx 0.965 \times 10^{-23}$ J/K. By the way, formula “ $S = k \log W$ ” is engraved on the tombstone of L. Boltzmann (1844-1906) who was the first one to recognize this intimate connection between the entropy and probability.

$$S \equiv \ln M. \quad (2.24a)$$

Using Eq. (20), we may recast this definition in the most frequently used form

Entropy
in
equilibrium

$$S = \ln \frac{1}{W_m} = -\ln W_m. \quad (2.24b)$$

(Again, please note that Eq. (24) is valid in the thermodynamic equilibrium only!)

Equation (24) satisfies the major condition for the entropy definition in thermodynamics, i.e. to be a unique characteristics of disorder. Indeed, according to Eq. (20), number M (and hence any function of M) are the only possible measures characterizing the microcanonical distribution. We also need this function of M to satisfy another requirement to the entropy, of being an extensive thermodynamic variable, and Eq. (24) does satisfy this requirement as well. Indeed, mathematics says that for two independent systems the joint probability is just a product of their partial probabilities, and hence, according to Eq. (24b), their entropies just add up.

Now let us see whether Eqs. (20) and (24) are compatible with the 2nd law of thermodynamics. For that, we need to generalize Eq. (24) for S to an arbitrary state of the system (generally, out of thermodynamic equilibrium), with arbitrary state probabilities W_m . For that, let us first recognize that M in Eq. (24) is just the number of possible ways to commit a particular system to a certain state n ($n = 1, 2, \dots, M$), in a statistical ensemble where each state is equally probable. Now let us consider a more general ensemble, still consisting of a large number $N \gg 1$ of similar systems, but with a certain number $N_m = W_m N \gg 1$ of systems in each of M states, with W_m not necessarily equal. In this case the evident generalization of Eq. (24) is that the entropy S_N of the whole ensemble is

$$S_N \equiv \ln M(N_1, N_2, \dots), \quad (2.25)$$

where $M(N_1, N_2, \dots)$ is the number of ways to commit a particular system to a certain state n , while keeping all numbers N_n fixed. Such number $M(N_1, N_2, \dots)$ is clearly equal to the number of ways to distribute N distinct balls between M different boxes, with the fixed number N_m of balls in each box, but in no particular order within it. Comparing this description with the definition of the so-called *multinomial coefficients*,¹¹ we get

$$M(N_1, N_2, \dots) = {}^N C_{N_1, N_2, \dots, N_M} \equiv \frac{N!}{N_1! N_2! \dots N_M!}, \quad \text{with } N = \sum_{m=1}^M N_m. \quad (2.26)$$

In order to simplify the resulting expression for S_N , we can use the famous *Stirling formula* in its crudest, de Moivre's form¹² whose accuracy is suitable for most purposes of statistical physics:

$$\ln(N!)_{|N \rightarrow \infty} \rightarrow N(\ln N - 1). \quad (2.27)$$

When applied to our current problem, this gives the following average entropy per system,¹³

¹¹ See, e.g., MA Eq. (2.3). Despite the intimidating name, Eq. (26) may be very simply derived. Indeed, $N!$ is just the number of all possible permutations of N balls, i.e. the ways to place them in *certain* positions – say, inside M boxes. Now in order to take into account that the particular order of the balls in each box is not important, that number should be divided by all numbers $N_n!$ of possible permutations of balls within each box – that's it.

¹² See, e.g., MA Eq. (2.10).

$$\begin{aligned}
S \equiv \frac{S_N}{N} &= \frac{1}{N} \ln \binom{N}{N_1, N_2, \dots, N_M} = \frac{1}{N} \left[\ln(N!) - \sum_{m=1}^M \ln(N_m!) \right] \\
&\xrightarrow{N_m \rightarrow \infty} \frac{1}{N} \left[N(\ln N - 1) - \sum_{m=1}^M N_m (\ln N_m - 1) \right] = \ln N - \frac{1}{N} \sum_{m=1}^M N_m \ln N_m = - \sum_{m=1}^M \frac{N_m}{N} \ln \frac{N_m}{N}.
\end{aligned} \tag{2.28}$$

and since this result is only valid in the limit $N_m \rightarrow \infty$ anyway, we may use Eq. (2) to present it as

$$S = - \sum_{m=1}^M W_m \ln W_m = \sum_{m=1}^M W_m \ln \frac{1}{W_m}. \tag{2.29}$$

Entropy
out of
equilibrium

This extremely important formula¹⁴ may be interpreted as the average of the entropy values given by Eq. (24), weighed with specific probabilities W_m in accordance with the general formula (7).¹⁵

Now let us find what distribution of probabilities W_m provides the largest value of entropy (29). The answer is almost evident from a single glance at Eq. (29). For example, if coefficients W_m are constant (and hence equal to $1/M'$) for a subgroup of $M' \leq M$ states and equal zero for all others, all M' nonvanishing terms in the sum (29) are equal to each other, so that

$$S = M' \frac{1}{M'} \ln M' = \ln M', \tag{2.30}$$

so that the closer M' to its maximum number M the larger S . Hence, the maximum of S is reached at the uniform distribution given by Eq. (24).

In order to prove this important fact more strictly, let us find the maximum of function given by Eq. (29). If its arguments $W_1, W_2, \dots, W_M$ were completely independent, this could be done by finding the point (in the M -dimensional space of coefficients W_m) where all partial derivatives $\partial S / \partial W_m$ are equal to zero. However, since the probabilities are constrained by condition (4), the differentiation has to be carried out more carefully, taking into account this interdependence:

$$\left[\frac{\partial}{\partial W_m} S(W_1, W_2, \dots) \right]_{\text{cond}} = \frac{\partial S}{\partial W_m} + \sum_{m' \neq m} \frac{\partial S}{\partial W_{m'}} \frac{\partial W_{m'}}{\partial W_m}. \tag{2.31}$$

At the maximum of function S , all such expressions should be equal to zero simultaneously. This condition may be presented as $\partial S / \partial W_m = \lambda$, where the so-called *Lagrange multiplier* λ is independent of m . Indeed, at such point Eq. (31) becomes

$$\left[\frac{\partial}{\partial W_m} S(W_1, W_2, \dots) \right]_{\text{cond}} = \lambda + \sum_{m' \neq m} \lambda \frac{\partial W_{m'}}{\partial W_m} = \lambda \left(\frac{\partial W_m}{\partial W_m} + \sum_{m' \neq m} \frac{\partial W_{m'}}{\partial W_m} \right) = \lambda \frac{\partial}{\partial W_m} (1) = 0. \tag{2.32}$$

¹³ Strictly speaking, I should use notation $\langle S \rangle$ here. However, following the style accepted in thermodynamics, I will drop the averaging sign until we will really need them to avoid confusion. Again, this shorthand is not too bad because the relative fluctuations of entropy (as those of any macroscopic variable) are very small at $N \gg 1$.

¹⁴ With the replacement of $\ln W_m$ for $\log_2 W_m$ (i.e. division by $\ln 2$), Eq. (29) is famous as the *Shannon* (or “Boltzmann-Shannon”) *formula* for average information I per symbol in a long communication string using M different symbols, with probability W_m each.

¹⁵ In some textbooks, this simple argument is even accepted as the derivation of Eq. (29); however, it is evidently less strict than the one outlined above.

For the particular expression (29), condition $\partial S/\partial W_m = \lambda$ yields

$$\frac{\partial S}{\partial W_m} \equiv \frac{d}{dW_m} [-W_m \ln W_m] = -\ln W_m - 1 = \lambda. \quad (2.33)$$

Equation (33) may hold for all m (and hence the entropy reach its maximum value) only if W_m is independent on m . Thus entropy (29) indeed reaches its maximum value (24) at equilibrium.

To summarize, we see that definition (24) of entropy in statistical physics does fit all the requirements imposed on this variable by thermodynamics.¹⁶ In particular, we have been able to prove the 2nd law of thermodynamics, starting from that definition and a more fundamental postulate (20). Now let me discuss one possible point of discomfort with that definition: it depends on the accepted energy interval of the microcanonical ensemble, for whose width ΔE no exact guidance is offered. However, if the interval ΔE contains many states, $M \gg 1$, then with a very small relative error (vanishing in the limit $M \rightarrow \infty$), M may be presented as

$$M = g(E)\Delta E, \quad (2.34)$$

where $g(E)$ is the *density of states* of the system:

$$g(E) \equiv \frac{d\Sigma(E)}{dE}, \quad (2.35)$$

$\Sigma(E)$ being the total number of states with energies *below* E . (Note that the average interval δE between energy levels, mentioned in the beginning of this section, is just $\delta E = \Delta E/M = 1/g$.) Plugging Eq. (34) into Eq. (24), we get

$$S = \ln M = \ln g(E) + \ln \Delta E, \quad (2.36)$$

so that the only effect of a particular choice of ΔE is an offset of entropy by a constant, and in Chapter 1 we have seen that such a shift does not affect any measurable quantity. Of course, Eq. (34), and hence Eq. (36) are only precise in the limit when density of states $g(E)$ is so large that the range available for the appropriate choice of ΔE ,

$$g^{-1}(E) \ll \Delta E \ll E, \quad (2.37)$$

is sufficiently broad: $M = g(E)E = E/\delta E \gg 1$.

In order to get some feeling of the functions $g(E)$ and $S(E)$ and the feasibility of condition (37), and also to see whether the microcanonical distribution may be directly used for calculations of thermodynamic variables in particular systems, let us apply it to a microcanonical ensemble of many sets of $N \gg 1$ independent, similar harmonic oscillators with eigenfrequency ω . (Please note that the requirement of a virtually fixed energy is applied, in this case, the total energy E_N of the set, rather to a single oscillator - whose energy E may be virtually arbitrary, though certainly less than $E_N \sim NE$.) Basic quantum mechanics¹⁷ teaches us that the eigenenergies of such an oscillator form a discrete, equidistant spectrum:

¹⁶ This is not to say that these definitions are fully equivalent. Despite all the wealth of quantitative relations given by thermodynamics, it still leaves a substantial uncertainty in the definition of entropy (and hence temperature), while Eq. (24) narrows this uncertainty to an unsubstantial constant.

¹⁷ See, e.g., QM Secs. 2.10 and 5.4.

$$E_m = \hbar\omega \left(m + \frac{1}{2} \right), \quad \text{where } m = 0, 1, 2, \dots \quad (2.38)$$

If ω is kept constant, the zero-point energy $\hbar\omega/2$ does not contribute to any thermodynamic properties of the system and may be ignored,¹⁸ so that for the sake of simplicity we may take that point as the energy origin, and replace Eq. (38) with $E_m = m\hbar\omega$. Let us carry out an approximate analysis of the system for the case when its average energy per oscillator,

$$E = \frac{E_N}{N}, \quad (2.39)$$

is much larger than the energy quantum $\hbar\omega$. For one oscillator, the number of states with energy ε_1 below certain value $= E_1 \gg \hbar\omega$ is evidently $\Sigma(E_1) \approx E_1/\hbar\omega$ (Fig. 3a). For two oscillators, all possible values of the total energy ($\varepsilon_1 + \varepsilon_2$) below some level E_2 correspond to the points of a 2D square grid within the right triangle shown in Fig. 3b, giving $\Sigma(E_2) \approx (1/2)(E_2/\hbar\omega)^2$. For three oscillators, the possible values of the total energy ($\varepsilon_1 + \varepsilon_2 + \varepsilon_3$) correspond to those points of the 3D cubic mesh, that fit inside the right pyramid shown in Fig. 3c, giving $\Sigma(E_3) \approx (1/2)(1/3)(E_3/\hbar\omega)^3 = (1/3!)(E_3/\hbar\omega)^3$, etc.

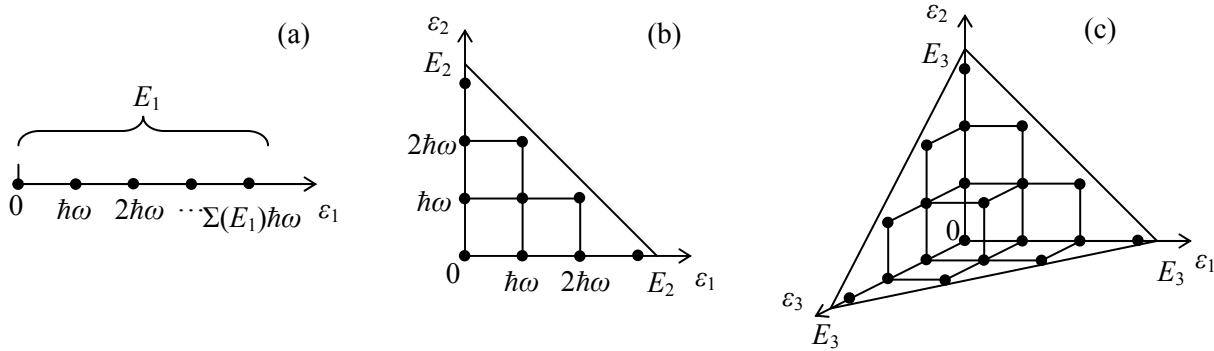


Fig. 2.3. Calculating functions $\Sigma(E_N)$ for the systems of (a) one, (b) two and (c) three quantum oscillators.

An evident generalization of these formulas to arbitrary N gives the number of states

$$\Sigma(E_N) \approx \frac{1}{N!} \left(\frac{E_N}{\hbar\omega} \right)^N, \quad (2.40)$$

where coefficient $1/N!$ has the geometrical meaning of the (hyper)volume of the N -dimensional right pyramid with unit sides. Differentiating Eq. (40), we get

$$g(E_N) = \frac{d\Sigma(E_N)}{dE_N} = \frac{1}{(N-1)!} \frac{E_N^{N-1}}{(\hbar\omega)^N}, \quad (2.41)$$

so that

¹⁸ Let me hope that the reader knows that the zero-point energy is experimentally measurable – for example using the famous *Casimir effect* - see, e.g., QM Sec. 9.1. In Sec. 5.6 below we will discuss another method of experimental observation of that energy.

$$S_N(E_N) = \ln g(E_N) + \text{const} = -\ln[(N-1)!] + (N-1)\ln E_N - N\ln(\hbar\omega) + \text{const}. \quad (2.42)$$

For $N \gg 1$ we can ignore the difference between N and $(N-1)$ in both instances, and use the Stirling formula (27) to simplify this result as

$$S_N(E) - \text{const} \approx N \left(\ln \frac{E_N}{N\hbar\omega} + 1 \right) \approx N \left(\ln \frac{E}{\hbar\omega} \right) = \ln \left[\left(\frac{E}{\hbar\omega} \right)^N \right]. \quad (2.43)$$

(The second approximation is only valid at very high $E/\hbar\omega$ ratios, when the logarithm in Eq. (43) is substantially larger than 1, i.e. is rather crude.¹⁹) Returning for a second to the density of states, we see that in the limit $N \rightarrow \infty$, it is exponentially large:

$$g(E_N) = e^{S_N} \approx \left(\frac{E}{\hbar\omega} \right)^N, \quad (2.44)$$

so that both conditions (37) may be satisfied within a very broad range of ΔE .

Now we can use Eq. (43) to find all thermodynamic properties of the system, though only in the limit $E \gg \hbar\omega$. Indeed, according to thermodynamics (see Sec. 1.2), if the system volume and number of particles are fixed, the derivative dS/dE is nothing more than the reciprocal temperature – see Eqs. (1.9) or (1.15). In our current case, we imply that the harmonic oscillators are distinct, for example by their spatial positions. Hence, even if we can speak of some volume of the system, it is certainly fixed.²⁰ Differentiating Eq. (43) over energy E , we get

Average
energy of a
classical
oscillator

$$\frac{1}{T} = \frac{dS_N}{dE_N} = \frac{N}{E_N} = \frac{1}{E}. \quad (2.45)$$

Reading this result backwards, we see that the average energy E of a harmonic oscillator equals T (i.e. $k_B T_K$ is SI units). As we will show in Sec. 5 below, this is the correct asymptotic form of the exact result, valid in our current limit $E \gg \hbar\omega$.

Result (45) may be readily generalized. Indeed, in quantum mechanics a harmonic oscillator with eigenfrequency ω may be described by Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{\kappa \hat{q}^2}{2}, \quad (2.46)$$

where q is some generalized coordinate, and p the corresponding generalized momentum, m is oscillator's mass,²¹ and κ is the spring constant, so that $\omega = (\kappa/m)^{1/2}$. Since in thermodynamic equilibrium the density matrix is always diagonal (see Sec. 1 above) in basis of stationary states m , quantum-mechanical averages of the kinetic and potential energies may be found from Eq. (7):

¹⁹ Let me offer a very vivid example how slowly does the logarithm function grow at large values of its argument: $\ln$ of the number of atoms in the visible Universe is less than 200.

²⁰ By the same reason, the notion of pressure P in such a system is not clearly defined, and neither are any thermodynamic potentials but E and F .

²¹ Let me hope that using the same letter for the mass and the state number would not lead to reader's confusion. I believe that the difference between these uses is very clear from the context.

$$\left\langle \frac{p^2}{2m} \right\rangle = \sum_{m=0}^{\infty} W_m \langle m | \frac{\hat{p}^2}{2m} | m \rangle, \quad \left\langle \frac{\kappa q^2}{2} \right\rangle = \sum_{m=0}^{\infty} W_m \langle m | \frac{\kappa \hat{q}^2}{2} | m \rangle, \quad (2.47)$$

where W_m is the probability to occupy m -th energy level, and bra- and ket-vectors describe the stationary state corresponding to that level.²² However, both classical and quantum mechanics teach us that for any m , the bra-kets under the sums in Eqs. (47), which present the average kinetic and mechanical energies of the oscillator on its m^{th} energy level, are equal to each other, and hence each of them is equal to $E_m/2$. Hence, even though we do not know the probability distribution W_m yet (it will be calculated in Sec. 5 below), we may conclude that in the “classical limit” $T \gg \hbar\omega$,

$$\boxed{\left\langle \frac{p^2}{2m} \right\rangle = \left\langle \frac{\kappa q^2}{2} \right\rangle = \frac{T}{2}}. \quad (2.48) \quad \text{Equipartition theorem}$$

Now let us consider a system with an arbitrary number of degrees of freedom, described by a more general Hamiltonian:²³

$$\hat{H} = \sum_j \hat{H}_j, \quad \hat{H}_j = \frac{\hat{p}_j^2}{2m_j} + \frac{\kappa_j \hat{q}_j^2}{2}, \quad (2.49)$$

with (generally, different) eigenfrequencies $\omega_j = (\kappa_j/m_j)^{1/2}$. Since the “modes” (effective harmonic oscillators), contributing into this Hamiltonian, are independent, result (48) is valid for each of the modes. This is the famous *equipartition theorem*: at thermal equilibrium with $T \gg \hbar\omega_j$, the average energy of each so-called *half-degree of freedom* (which are defined as variables p_j or q_j , giving a quadratic term to the system’s Hamiltonian), is equal to $T/2$.²⁴ In particular, for each Cartesian coordinate q_j of a free-moving, non-interacting particle this theorem is valid for *any* temperature, because such coordinates may be considered as 1D harmonic oscillators with vanishing potential energy, i.e. $\omega_j = 0$, so that condition $T \gg \hbar\omega_j$ is fulfilled at any temperature.

At this point, a first-time student of thermodynamics should be very much relieved to see that the counter-intuitive thermodynamic definition (1.9) of temperature does indeed correspond to what we all have known about this notion from our kindergarten physics courses.

I believe that our case study of quantum oscillator systems has been a fair illustration of both the strengths and weaknesses of the microcanonical ensemble approach.²⁵ On one hand, we could calculate virtually everything we wanted in the classical limit $T \gg \hbar\omega$, but calculations for arbitrary $T \sim \hbar\omega$, though possible, are difficult, because for that, all vertical steps of function $\Sigma(E_N)$ have to be carefully

²² Note again that though we have committed the energy E_N of N oscillators to be fixed (in order to apply Eq. (36), valid only for a microcanonical ensemble at thermodynamic equilibrium), single oscillator’s energy E in our analysis may be arbitrary - within limits $\hbar\omega \ll E < E_N \sim NT$.

²³ As a reminder, the Hamiltonian of any system whose classical Lagrangian function is an arbitrary quadratic form its generalized coordinates and the corresponding generalized velocities, may be brought to form (49) by an appropriate choice of “normal coordinates” q_j which are certain linear combinations of the original coordinates – see, e.g., CM Sec. 5.2.

²⁴ This also means that in the classical limit, the heat capacity of a system is equal to the number of its half-degrees of freedom (in SI units, multiplied by k_B).

²⁵ The reader is strongly urged to solve Exercise 2, whose task is to do a similar calculation for another key (“two-level”) physical system, and to compare the results.

counted. In Sec. 4, we will see that other statistical ensembles are much more convenient for such calculations.

Let me conclude this discussion of entropy with a short notice on deterministic classical systems with a few degrees of freedom (and even simpler mathematical objects called “maps”) that may exhibit essentially disordered behavior, called the *deterministic chaos*.²⁶ Such chaotic system may be approximately characterized by an entropy defined similarly to Eq. (29), where W_m are probabilities to find it in different small regions of phase space, at well separated time intervals. On the other hand, one can use an equation slightly more general than Eq. (29) to define the so-called *Kolmogorov* (or “Kormogorov-Sinai”) *entropy* K that characterizes the speed of loss of information about the initial state of the system, and hence what is called the “chaos’ depth”. In the definition of K , the sum over m is replaced with the summation over all possible permutations $\{m\} = m_0, m_1, \dots, m_{N-1}$ of small space regions, and W_m is replaced with $W_{\{m\}}$, the probability of finding the system in the corresponding regions m at time moment t_m , with $t_m = m\tau$, in the limit $\tau \rightarrow 0$, with $N\tau = \text{const}$. For chaos in the simplest objects, 1D maps, K is equal to the Lyapunov exponent $\lambda > 0$.²⁷ For systems of higher dimensionality, which are characterized by several Lyapunov exponents λ , the Kolmogorov entropy is equal to the phase-space average of the sum of all positive λ . These facts provide a much more practicable way of (typically, numerical) calculation of the Kolmogorov entropy than the direct use of its definition.²⁸

2.3. Maxwell’s Demon, information, and computation

Before proceeding to other statistical distributions, I would like to address one more popular concern about Eq. (24), the direct relation between the entropy and information. Some physicists are still uneasy with entropy being nothing else than the (deficit of) information,²⁹ though to the best of my knowledge, nobody has yet been able to suggest any experimentally verifiable difference between these two notions. Let me give one example of their direct relation, that is essentially a development of the thought experiment suggested by Maxwell as early as in 1867.

Consider a volume containing just one molecule (considered as a point particle), and separated to two equal halves by a movable partition with a door that may be opened and closed at will, at no energy cost (Fig. 4a). If the door is open and the system is in thermodynamic equilibrium, we do not know on which side of the door partition the molecule is. Here the disorder (and hence entropy) are largest, and there is no way to get, from a large ensemble of such systems, any useful mechanical energy.

Now, let us consider that we (as instructed by, in Lord Kelvin’s formulation, an omniscient *Maxwell’s Demon*) know which side of the partition the molecule is currently located. Then we may

²⁶ See, e.g., CM Chapter 9 and literature therein.

²⁷ For the definition of λ , see, e.g., CM Eq. (9.9).

²⁸ For more discussion, see, e.g., either Sec. 6.2 of the monograph H. G. Schuster and W. Just, *Deterministic Chaos*, 4th ed., Wiley-VHS, 2005, or the monograph by Arnold and Avez, cited in Sec. 1.

²⁹ While some of these concerns should be treated with due respect (because the ideas of entropy and disorder are indeed highly nontrivial), I have repeatedly run into rather shallow arguments which stemmed from arrogant contempt to the information theory as an “engineering discipline”, and unwillingness to accept the notion of information on the equal footing with those of space, time, and energy. Fortunately, most leading physicists are much more flexible, and there are even opposite extremes such as J. A. Wheeler’s “it from bit” (i.e. matter from information) philosophy – to which I cannot fully subscribe either.

close the door, so that molecule's impacts on the partition create, on the average, a pressure force $\vec{f}$ directed toward the empty part of the volume (in Fig. 4b, the right one). Now we can get from the molecule some mechanical work, say by allowing force $\vec{f}$ to move the partition to the right, and picking up the resulting mechanical energy by some deterministic external mechanism. After the partition has been moved to the right end of the volume, we can open the door again (Fig. 4c), equalizing the molecule's average pressure on both sides of the partition, and then slowly move the partition back to the middle of the volume, without doing any substantial work. With the kind help by Maxwell's Demon, we can repeat the cycle again and again, and hence make the system to do unlimited mechanical work, fed "only" by information and thermal motion, and thus implementing the perpetual motion machine of the 2nd kind – see Sec. 1.6. The fact that such heat engines do not exist means that the Maxwell's Demon does not either: getting any *new* information, at nonvanishing temperature (i.e. at thermal agitation of particles) has a finite energy cost.

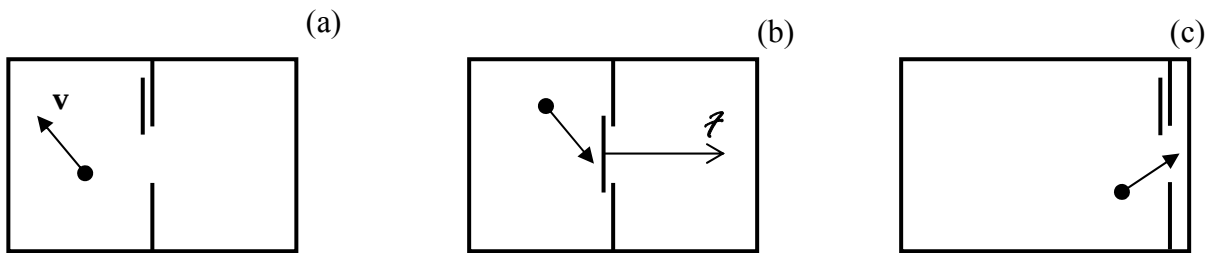


Fig. 2.4. The Maxwell's Demon paradox: the volume with a single molecule (a) before and (b) after closing the door, and (c) after opening the door in the end of the expansion stage.

In order to evaluate this cost, let us calculate the maximum work per cycle made by the Maxwell's heat engine (Fig. 4), assuming that it is constantly in thermal equilibrium with a heat bath of temperature T . Formula (21) tells us that the information supplied by the demon (what exactly half of the volume contains the molecule) is exactly one bit, $I(2) = 1$. According to Eq. (24), this means that by getting this information we are reducing entropy by $\Delta S_I = -\ln 2$. Now, it would be a mistake to plug this (negative) entropy change into Eq. (1.19). First, that relation is only valid for slow, reversible processes. Moreover (and more importantly), this equation, as well as its irreversible version (1.41), is only valid for a fixed statistical ensemble. The change ΔS_I does not belong to this category, and may be formally described by the change of the statistical ensemble – from the one consisting of all similar systems (experiments) with an unknown location of the molecule, to the new ensemble consisting of the systems with the molecule in its certain (in Fig. 4, left) half.³⁰

Now let us consider the slow expansion of the "gas" after the door had been closed. At this stage, we do not need the demon's help any longer (i.e. the statistical ensemble is fixed), and we can use relation (1.19). At the assumed isothermal conditions ($T = \text{const}$), this relation may be integrated over the whole expansion process, getting $\Delta Q = T\Delta S$. At the finite position, the system's entropy should be the same as initially, i.e. before the door had been opened, because we again do not know where in the volume the molecule is. This means that the entropy was replenished, during the reversible expansion,

³⁰ This procedure of *redefining the statistical ensemble* is the central point of the connection between the information theory and physics, and is crucial in particular for any (meaningful :-) discussion of measurements in quantum mechanics - see, e.g., QM Secs. 2.5 and 7.7.

from the heat bath, by $\Delta S = -\Delta S_I = +\ln 2$, so that $\Delta Q = T\Delta S = T\ln 2$. Since by the end of the whole cycle the internal energy E of the system is the same as before, all this heat should have gone into the mechanical energy obtained during the expansion. Thus the obtained work per cycle (i.e. for each obtained information bit) is $T\ln 2$ ($k_B T_K \ln 2$ in SI units), about 4×10^{-21} Joule at room temperature. This is exactly the minimum energy cost of getting one bit of *new* information about a system at temperature T .

The smallness of that amount on the everyday human scale has left the Maxwell's Demon paradox an academic exercise for almost a century. However, its discussion resumed in the 1960s in the context of energy consumption at numerical calculations, motivated by the exponential (*Moore's-law*) progress of the digital integrated circuits, which leads in particular, to a fast reduction of energy ΔE "spent" (turned into heat) per one binary logic operation. In the current generations of semiconductor digital integrated circuits, ΔE is of the order of $\sim 10^{-16}$ J,³¹ i.e. still exceeds the room-temperature value of $T\ln 2 = k_B T_K \ln 2 \approx 3 \times 10^{-21}$ J by more than 4 orders of magnitude. Still, some engineers believe that thermodynamics imposes an important lower limit on ΔE and hence presents an insurmountable obstacle to the future progress of computation,³² so that the issue deserves a discussion.

Let me believe that the reader of these notes understands that, in contrast to naïve popular thinking, computers do not *create* any new information; all they can do it to reshape (process) it, *losing* most of input information on the go. Indeed, any digital computation algorithm may be decomposed into simple, binary logical operations, each of them performed by a certain logic circuit called the *logic gate*. Some of these gates (e.g., logical NOT performed by inverters, as well as memory READ and WRITE operations) do not change the amount of information in the computer. On the other hand, such *information-irreversible* logic gates as two-input NAND (or NOR, or XOR, etc.) actually erase one bit at each operation, because they turn two input bits into one output bit (Fig. 5a).

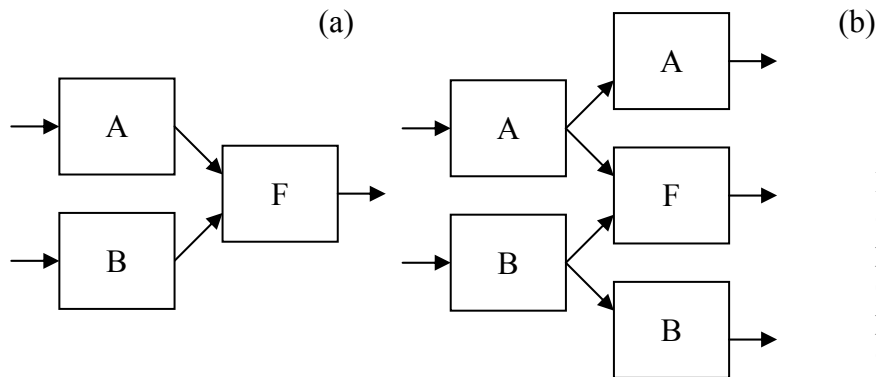


Fig. 2.5. Simple examples of (a) irreversible and (b) potentially reversible logic circuits. Each rectangle presents a circuit storing one bit of information.

In 1961, R. Landauer arrived at the conclusion that each logic operation should turn into heat at least energy

³¹ In the dominating *CMOS technology*, ΔE is close to twice the energy $CV^2/2$ of recharging the total capacitance C of the transistor gate electrodes and the wires interconnecting the gates, by the voltage V representing the binary unity. As the technology progresses, C decreases in approximate proportion with the minimum feature size, resulting in the almost proportional decrease of ΔE . (The used voltage V has almost saturated at ~ 1 V – the value that stems from the bandgap of ~ 1 eV of the used semiconductor – silicon.)

³² Unfortunately, this delusion has resulted in a substantial and unjustified shift of electron device research resources toward using “non-charge degrees of freedom” (such as spin) – as if they do not obey the general laws of statistical physics!

$$\Delta E_{\min} = T \ln 2 = k_B T_K \ln 2. \quad (2.51)$$

Energy
dissipation at
irreversible
computation

This result may be illustrated with the Maxwell's Demon machine shown in Fig. 4, operating as heat pump. At the first stage, with the door closed, it uses external mechanical work $\Delta E = T \ln 2$ to reduce the volume in which of the molecule is confined from V to $V/2$, pumping heat $-\Delta Q = \Delta E$ into the heat bath. To model a logically-irreversible logic gate, let us now open the door in the partition, and thus loose 1 bit of information about molecule's position. Then we will never get work $T \ln 2$ back, because moving the partition back to the right, with door open, takes place at zero average pressure. Hence, Eq. (51) gives a fundamental limit for energy loss (per bit) at the logically irreversible computation.

However, in 1973 C. Bennett came up with convincing arguments that it is possible to avoid such energy loss by using only operations that are *reversible* not only physically, but also logically.³³ For that, one has to avoid any loss of information, i.e. any erasure of intermediate results, for example in the way shown in Fig. 5b. (For that, gate F should be *physically reversible*, with no substantial static power consumption.) In the end of all calculations, after the result has been copied into a memory, the intermediate results may be “rolled back” through reversible gate to be eventually merged into a copy of input data, again without erasing a single bit. The minimal energy dissipation at such reversible calculation tends to zero as the operation speed is decreased, so that the average energy loss per bit may be less than the perceived “fundamental thermodynamic limit” (51).³⁴ The price to pay for this ultralow dissipation is an enormous (exponential) complexity of hardware necessary for storage of all intermediate results. However, using irreversible gates sparingly, it may be possible to reduce the complexity dramatically, so that in future the *mostly* reversible computation may be able to reduce energy consumption in practical digital electronics.³⁵

Before we leave Maxwell's Demon behind, let me use it to discuss, for one more time, the relation between the reversibility of the classical and quantum mechanics of Hamiltonian systems and the irreversibility possible in thermodynamics and statistical physics. In our (or rather Lord Kelvin's :-)) gedanken experiment shown in Fig. 4, the laws of mechanics governing the motion of the molecule are reversible all times. Still, at partition's motion to the right, driven by molecule's impacts, the entropy grows, because the molecule picks up heat $\Delta Q > 0$, and hence entropy $\Delta S = \Delta Q/T > 0$, from the heat bath. The physical mechanism of this irreversible entropy (read: disorder) growth is the interaction of the molecule with uncontrollable components of the heat bath, and the resulting loss of information about the motion of the molecule. Philosophically, the emergence of irreversibility in large systems is a strong argument against the *reductionism* – a naïve belief that knowing the exact laws of Nature at one level of its complexity, we can readily understand all the phenomena on the higher levels of its organization. In reality, the macroscopic irreversibility of large systems is a wonderful example of a new law (in this case, the 2nd law of thermodynamics) that becomes relevant on the substantially new level of complexity - without defying the lower-level laws. Without such new laws, very little of the higher level organization of Nature may be understood.

³³ C. Bennett, *IBM J. Res. Devel.* **17**, 525 (1973); see also a later review C. Bennett, *Int. J. Theor. Phys.* **21**, 905 (1982). To the best of my knowledge, the sub- $T \ln 2$ energy loss per logic step is still to be demonstrated experimentally, but at least one research team is closing at this goal.

³⁴ Reversible computation may also overcome the perceived “fundamental quantum limit”, $\Delta E \Delta t > \hbar$, where Δt is the time scale of the binary logic operation – see K. Likharev, *Int. J. Theor. Phys.* **21**, 311 (1982).

³⁵ The situation is rather different for *quantum computation* which may be considered as a specific type of reversible but *analog* computation – see, e.g., QM Sec. 8.5 and references therein.

2.4. Canonical ensemble and the Gibbs distribution

As we have seen in Sec. 2, the microcanonical distribution may be directly used for solving some simple problems,³⁶ but a further development of this approach (also due to J. Gibbs) turns out to be much more convenient for calculations. Let us consider that a statistical ensemble of similar systems we are studying, each in thermal equilibrium with a much larger heat bath of temperature T (Fig. 6a). Such an ensemble is called *canonical*.

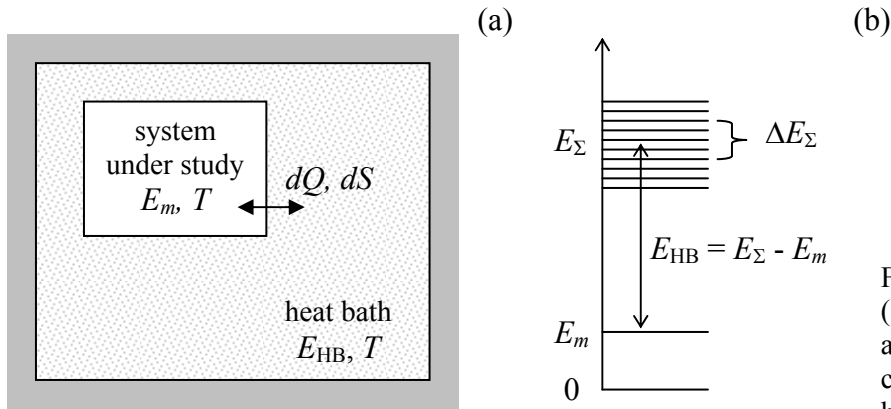


Fig. 2.6. (a) System in a heat bath (a canonical ensemble member) and (b) energy spectrum of the composite system (including the heat bath).

Next, it is intuitively evident that if the heat bath is sufficiently large, any thermodynamic variables characterizing the system under study should not depend on *heat bath's* environment. In particular, we may assume that the heat bath is thermally insulated; then the total energy E_Σ of the *composite system* (consisting of the system of our interest, plus the heat bath) does not change in time. For example, if our system of interest is on its certain (say, m^{th}) energy level, then

$$E_\Sigma = E_m + E_{\text{HB}} \quad (2.52)$$

is conserved. Now let us partition this *canonical* ensemble into much smaller sub-ensembles, each being a *microcanonical* ensemble of composite systems whose total energy E_Σ is the same - as discussed in Sec. 2, within a certain small energy interval $\Delta E_\Sigma \ll E_\Sigma$. According to the microcanonical distribution, probabilities to find the composite system, within this new ensemble, in any state are equal. Still, heat bath energies $E_{\text{HB}} = E_\Sigma - E_m$ (Fig. 6b) of members of this microcanonical sub-ensemble may be different due to the difference in E_m .

The probability $W(E_m)$ to find the system of our interest (within the selected sub-ensemble) on some energy level E_m is proportional to the number ΔM of such systems in the sub-ensemble. Due to the very large size of the heat bath in comparison with that of the system under study, the heat bath' density of states g_{HB} is very high, and ΔE_Σ may be selected so that

$$\frac{1}{g_{\text{HB}}} \ll \Delta E_\Sigma \ll |E_m - E_{m'}| \ll E_{\text{HB}}, \quad (2.53)$$

where m and m' are any states of the system of our interest. As Fig. 6b shows, in this case we may write $\Delta M = g_{\text{HB}}(E_{\text{HB}})\Delta E_\Sigma$. As a result, within the microcanonical ensemble with the total energy E_Σ ,

³⁶ See also exercise problems listed in the end of this chapter.

$$W_m \propto \Delta M = g_{\text{HB}}(E_{\text{HB}})\Delta E_{\Sigma} = g_{\text{HB}}(E_{\Sigma} - E_m)\Delta E_{\Sigma}. \quad (2.54)$$

Let us simplify this expression further, using the Taylor expansion with respect to relatively small $E_m \ll E_{\Sigma}$. However, here we should be careful. As we have seen in Sec. 2, the density of states of a large system is an extremely rapidly growing function of energy, so that if we applied the Taylor expansion directly to Eq. (54), the Taylor series would converge for very small E_m only. A much broader applicability range may be obtained by taking logarithm of both parts of Eq. (54) first:

$$\ln W_m = \text{const} + \ln[g_{\text{HB}}(E_{\Sigma} - E_m)] + \ln \Delta E_{\Sigma} = \text{const} + S_{\text{HB}}(E_{\Sigma} - E_m), \quad (2.55)$$

where the second equality results from application of Eq. (36) to the heat bath, and $\ln \Delta E_{\Sigma}$ has been incorporated into the constant. Now, we can Taylor-expand the (much more smooth) function of energy in the right-hand part, and limit ourselves to the two leading terms of the series:

$$\ln W_m \approx \text{const} + S_{\text{HB}} \Big|_{E_m=0} - \frac{dS_{\text{HB}}}{dE_{\text{HB}}} \Big|_{E_m=0} E_m. \quad (2.56)$$

But according to Eq. (1.9), the derivative participating in this expression is nothing else than the reciprocal heat bath temperature that (due to the large bath size) does not depend on whether E_m is equal to zero or not. Since our system of interest is in the thermal equilibrium with the bath, this is also the temperature T of the system – see Eq. (1.8). Hence Eq. (56) is merely

$$\ln W_m = \text{const} - \frac{E_m}{T}. \quad (2.57)$$

This equation describes a substantial decrease of W_m as E_m is increased by several T , and hence our linear approximation (56) is virtually exact as soon as E_{HB} is much larger than T – the condition that is rather easy to satisfy, because as we have seen in Sec. 2, the average energy of each particle is of the order of T .

Now we should be careful again, because so far we have only derived Eq. (57) for a sub-ensemble with fixed E_{Σ} . However, since the right-hand part of Eq. (57) includes only E_m and T that are independent of E_{Σ} , this relation is valid for all sub-ensembles of the canonical ensemble, and hence for the later ensemble as the whole.³⁷ Hence for the total probability to find our system of interest in state with energy E_m , in the canonical ensemble with temperature T , we can write

$$W_m = \text{const} \times \exp\left\{-\frac{E_m}{T}\right\} \equiv \frac{1}{Z} \exp\left\{-\frac{E_m}{T}\right\}. \quad (2.58)$$

Gibbs
distribution

This is the famous *Gibbs distribution* (sometimes called the “canonical distribution”),³⁸ which is frequently arguably the summit of statistical physics,³⁹ because it may be used for a straightforward (or at least conceptually straightforward :-) calculation of all statistical and thermodynamic variables.

³⁷ Another way to arrive at the same conclusion is to note that the entropy of the whole canonical ensemble with fixed E_m has to be a sum of entropies of its microcanonical sub-ensembles (with different E_{Σ}), which participate in Eq. (55). As a result, the logarithm of probability W_m for our system of interest to have energy E_m in the whole (canonical) ensemble is just a sum of Eqs. (57) for sub-ensembles with different E_{Σ} .

³⁸ The temperature dependence of the type $\exp\{-E/T\}$, especially when showing up in rates of certain events, e.g., chemical reactions, is also frequently called the *Arrhenius law* - after chemist S. Arrhenius who has noticed this

Before I illustrate this, let me first calculate the coefficient Z participating in Eq. (58) for the general case. Requiring, in accordance with Eq. (4), the sum of all W_m to be equal 1, we get

$$Z = \sum_m \exp\left\{-\frac{E_m}{T}\right\}, \quad (2.59)$$

Statistical
sum

where the summation is formally extended to all quantum states of the system, though in practical calculations, the sum may be truncated to include only the states that are noticeably occupied. This apparently humble normalization coefficient Z turns out to be so important for the relation between the Gibbs distribution (i.e. statistics) and thermodynamics that it has a special name - or actually, two names: either the *statistical sum* or the *partition function*. To demonstrate how important Z is, let us use the general Eq. (29) for entropy to calculate its value for the particular case of the canonical ensemble, i.e. the Gibbs distribution of probabilities W_n :

$$S = -\sum_m W_m \ln W_m = \frac{\ln Z}{Z} \sum_m \exp\left\{-\frac{E_m}{T}\right\} + \frac{1}{ZT} \sum_m E_m \exp\left\{-\frac{E_m}{T}\right\}. \quad (2.60)$$

According to the general rule (7), the thermodynamic (i.e. ensemble-average) value E of the internal energy of the system is

$$E = \sum_m W_m E_m = \frac{1}{Z} \sum_m E_m \exp\left\{-\frac{E_m}{T}\right\}, \quad (2.61a)$$

so that the second term in the right-hand part of Eq. (60) is just E/T , while the first term equals just $\ln Z$, due to the normalization condition (59). (As a parenthetic remark, using the notion of *reciprocal temperature* $\beta \equiv 1/T$, Eq. (61a), with account of Eq. (59), may be also rewritten as

$$E = -\frac{\partial(\ln Z)}{\partial \beta}. \quad (2.61b)$$

This formula is very convenient for calculations if our prime interest is the average energy E rather than F or W_n .) With these substitutions, Eq. (60) yields a very simple relation between the statistical sum and entropy:

$$S = \frac{E}{T} + \ln Z. \quad (2.62)$$

Using Eq. (1.33), we see that Eq. (62) gives a straightforward way to calculate the free energy F of the system from nothing else than its statistical sum:

$$F \equiv E - TS = T \ln \frac{1}{Z}. \quad (2.63)$$

F from Z

law in experimental data. In all cases I am aware of, the Gibbs distribution is the underlying reason of the Arrhenius law.

³⁹ This opinion is shared by several authoritative colleagues, including R. Feynman who climbs on this summit already by page 4 (!) of his brilliant book *Statistical Mechanics*, 2nd ed., Westview, 1998. (Despite its title, this monograph a collection of lectures on a few diverse, mostly advanced topics of statistical physics, rather than its systematic course, so that unfortunately I cannot recommend it as a textbook.)

Now, using the general thermodynamic relations (see especially the circular diagram shown in Fig. 1.7b, and its discussion) we can calculate all thermodynamic potentials of the system, and all other variables of interest. Let me only note that in order to calculate pressure P - e.g., from the second of Eqs. (1.35) - we would need to know the explicit dependence of F , and hence of the statistical sum Z on the system volume V . This would require the calculation, by appropriate methods of either classical or quantum mechanics, of the volume dependence of eigenenergies E_m . I will give numerous examples of such calculations later in the course.⁴⁰

As the final note of this section, Eqs. (59) and (63) may be combined to give a very elegant expression,

$$\exp\left\{-\frac{F}{T}\right\} = \sum_m \exp\left\{-\frac{E_m}{T}\right\}, \quad (2.64)$$

which offers a convenient interpretation of free energy as a (rather specific) average of eigenenergies of the system. One more convenient formula may be obtained by using Eq. (64) to rewrite the Gibbs distribution (58) in the form

$$W_m = \exp\left\{\frac{F - E_m}{T}\right\}. \quad (2.65)$$

In particular, this expression shows that that since all probabilities W_m are below 1, F is always lower than the lowest energy level. Also, note that probabilities W_m do not depend on the energy reference choice, i. e. on an arbitrary constant added to all E_m (and hence to E and F).

2.5. Harmonic oscillator statistics

The last property may be immediately used in our first example of the Gibbs distribution application to a particular, but very important system - the harmonic oscillator, for the more general case then was done in Sec. 2, namely for a “quantum oscillator” with an arbitrary relation between T and $\hbar\omega$.⁴¹ Let us consider a canonical ensemble of similar oscillators, each in a contact with a heat bath of temperature T . Selecting the zero-point energy $\hbar\omega/2$ for the origin of E , oscillator eigenenergies (38) become $E_m = m\hbar\omega$ ($m = 0, 1, \dots$), so that the Gibbs distribution for probabilities of these states is

$$W_m = \frac{1}{Z} \exp\left\{-\frac{E_m}{T}\right\} = \frac{1}{Z} \exp\left\{-\frac{m\hbar\omega}{T}\right\}, \quad (2.66)$$

⁴⁰ In many multiparticle systems, the effect of an external field may be presented as a sum of its effects on each particle - frequently described by interaction energy with structure $-\mathcal{J}_j q_j^{(k)}$, where $q_j^{(k)}$ is a generalized coordinate of k -th particle. Generally, this energy has to be included directly into energies of particle states E_m , used in Z , and hence in the free energy F (63). In this case, the thermodynamic equilibrium corresponds to the minimum of F - see Eq. (1.42). On the other hand, for “linear” systems (whose energy is a quadratic-homogeneous form of its generalized coordinates and velocities), equivalent results may be obtained by accounting for the interaction at the thermodynamic level, i.e. by subtracting term $\mathcal{J}_j \langle q_j \rangle = \mathcal{J}_j N \langle q_j^{(k)} \rangle$ from the free energy F calculated in the absence of the field, and then finding the equilibrium as a minimum of the resulting Gibbs energy G - see Eq. (1.43). In this case, any of the approaches is fine, provided only that the same interaction is not counted twice.

⁴¹ A simpler task of making a similar calculation for another key quantum-mechanical object, the two-level system, is left for reader’s exercise.

with the statistical sum

$$Z \equiv \sum_{m=0}^{\infty} \exp\left\{-\frac{m\hbar\omega}{T}\right\} = \sum_{m=0}^{\infty} \lambda^m, \quad \text{where } \lambda \equiv \exp\left\{-\frac{\hbar\omega}{T}\right\} \leq 1. \quad (2.67)$$

This series is just an infinite geometric progression (“geometric series”); summing it,⁴² we get

$$Z = \frac{1}{1-\lambda} = \frac{1}{1-e^{-\hbar\omega/T}}, \quad (2.68)$$

Quantum
oscillator's
statistics

so that for the probability W_m to find the oscillator at each energy level is

$$W_m = (1 - e^{-\hbar\omega/T}) e^{-m\hbar\omega/T}. \quad (2.69)$$

As Fig. 7a shows, the probability W_m to find the oscillator in each particular state (but the ground one, with $m = 0$) vanishes in both low- and high-temperature limits, and reaches its maximum value $W_m \sim 0.3/m$ at $T \sim m\hbar\omega$, so that the contribution $m\hbar\omega W_n$ of each level into the average oscillator energy E is always smaller than $\hbar\omega$.

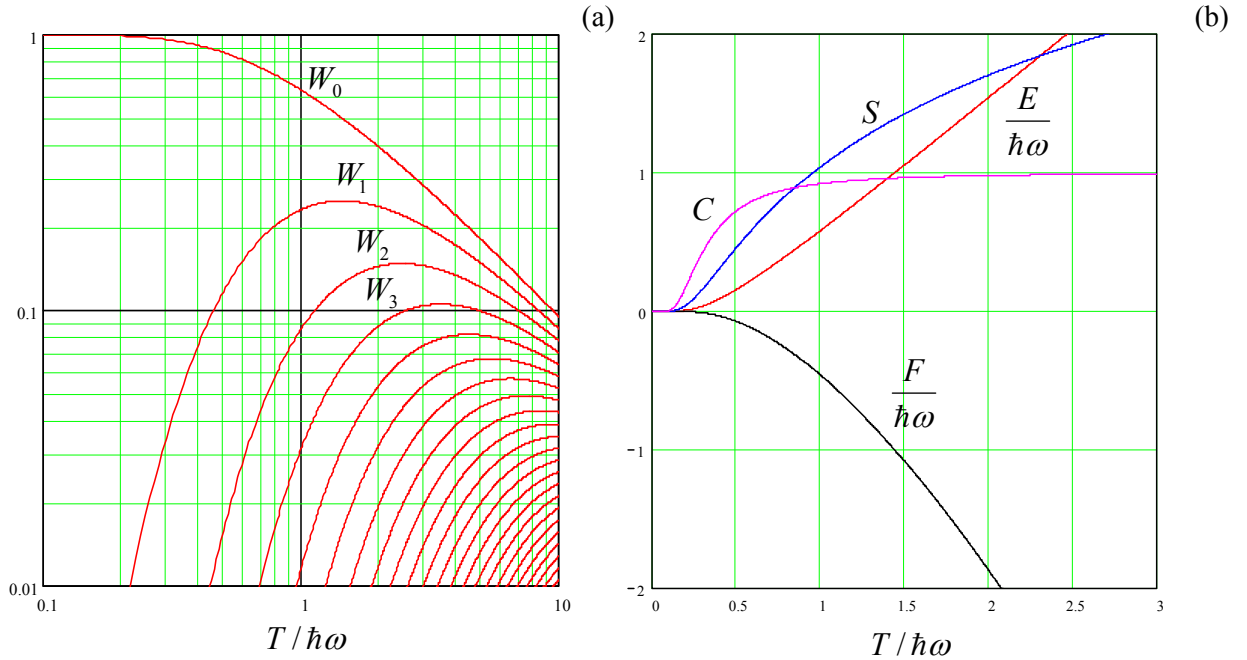


Fig. 2.7. Statistical and thermodynamic parameters of a harmonic oscillator, as functions of temperature.

This average energy may be calculated in any of two ways: either using Eq. (7):

$$E = \sum_{m=0}^{\infty} E_m W_m = (1 - e^{-\hbar\omega/T}) \sum_{m=0}^{\infty} m\hbar\omega e^{-m\hbar\omega/T}, \quad (2.70)$$

or (simpler) using Eq. (61b), as

⁴² See, e.g., MA Eq. (2.8b).

$$E = -\frac{\partial}{\partial \beta} \ln Z = \frac{\partial}{\partial \beta} \ln(1 - \exp\{-\beta \hbar \omega\}), \quad \beta \equiv \frac{1}{T}. \quad (2.71)$$

Both methods give (of course) the same famous result,⁴³

$$E = E(\omega, T) = \hbar \omega \frac{1}{e^{\hbar \omega / T} - 1}, \quad (2.72)$$

Quantum
oscillator's
average
energy

which is valid for arbitrary temperature and plays the key role in many fundamental problems of physics. The red line in Fig. 7b shows this E as a function of normalized temperature. At low temperatures, $T \ll \hbar \omega$, the oscillator is predominantly in its lowest (ground) state, and its energy (on top of the constant zero-point energy $\hbar \omega / 2$!) is exponentially small: $E \approx \hbar \omega \exp\{-\hbar \omega / T\} \ll T, \hbar \omega$. On the other hand, in the high-temperature limit the energy tends to T . This is exactly the result (a particular case of the equipartition theorem) that was obtained in Sec. 2 from the microcanonical distribution. Please note how much simpler is the calculation starting from the Gibbs distribution, even for an arbitrary ratio $T / \hbar \omega$.

To complete the discussion of thermodynamic properties of the harmonic oscillator, we can calculate its free energy using Eq. (63):

$$F = T \ln \frac{1}{Z} = T \ln(1 - e^{-\hbar \omega / T}). \quad (2.73)$$

Now entropy may be found from thermodynamics: either from the first of Eqs. (1.35), $S = -(\partial F / \partial T)_V$, or (even more easily) from Eq. (1.33): $S = (E - F) / T$. Both relations give, of course, the same result:

$$S = \frac{\hbar \omega}{T} \frac{1}{e^{\hbar \omega / T} - 1} - \ln(1 - e^{-\hbar \omega / T}). \quad (2.74)$$

Finally, since in the general case the dependence of the oscillator properties (essentially, ω) on volume V in this problem is not specified, such variables as P , μ , G , W , and Ω are not defined, and we may calculate only the average heat capacity C per one oscillator:

$$C = \frac{\partial E}{\partial T} = \left(\frac{\hbar \omega}{T} \right)^2 \frac{e^{\hbar \omega / T}}{(e^{\hbar \omega / T} - 1)^2} = \left[\frac{\hbar \omega / 2T}{\sinh(\hbar \omega / 2T)} \right]^2. \quad (2.75)$$

The calculated thermodynamic variables are shown in Fig. 7b. In the low-temperature limit ($T \ll \hbar \omega$), they all tend to zero. On the other hand, in the high temperature limit ($T \gg \hbar \omega$), $F \rightarrow -T \ln(T / \hbar \omega) \rightarrow -\infty$, $S \rightarrow \ln(T / \hbar \omega) \rightarrow +\infty$, and $C \rightarrow 1$ (in SI units, $C \rightarrow k_B$). Note that the last limit is the direct corollary of the equipartition theorem: each of two “half-degrees of freedom” of the oscillator gives, in the classical limit, a contribution $C = 1/2$ into its heat capacity.

Now let us use Eq. (69) to discuss the statistics of the quantum oscillator described by Hamiltonian (46), in the coordinate representation. Again using density matrix’ diagonality at thermodynamic equilibrium, we may use a relation similar to Eqs. (47) to calculate the probability density to find the oscillator at coordinate q :

⁴³ It was first obtained in 1924 by S. Bose, and is frequently called the *Bose distribution* – a particular case of the *Bose-Einstein distribution* – to be discussed in Sec. 8 below.

$$w(q) = \sum_{m=0}^{\infty} W_m w_m(q) = \sum_{m=0}^{\infty} W_m |\psi_m(q)|^2 = \left(1 - e^{-\hbar\omega/T}\right) \sum_{m=0}^{\infty} e^{-m\hbar\omega/T} |\psi_m(q)|^2, \quad (2.76)$$

where $\psi_m(q)$ is the eigenfunction of m -th stationary state of the oscillator. Since each $\psi_m(q)$ is proportional to the Hermite polynomial⁴⁴ that requires at least m elementary functions for its representation, working out the sum in Eq. (76) is a bit tricky,⁴⁵ but the final result is rather simple: $w(q)$ is just a normalized *Gaussian distribution* (the “bell curve”),

$$w(q) = \frac{1}{(2\pi)^{1/2} \delta q} \exp\left\{-\frac{q^2}{2(\delta q)^2}\right\}, \quad (2.77)$$

with $\langle q \rangle = 0$, and

$$\langle q^2 \rangle = \frac{\hbar}{2m\omega} \coth \frac{\hbar\omega}{2T}. \quad (2.78)$$

Since $\coth \xi$ tends to 1 at $\xi \rightarrow \infty$, and diverges as $1/\xi$ at $\xi \rightarrow 0$, Eq. (78) shows that the width of coordinate distribution is constant (and equal to that, $\hbar/2m\omega$, of the ground-state wavefunction ψ_0) at $T \ll \hbar\omega$, and grows as $T/m\omega^2$ at $T/\hbar\omega \rightarrow \infty$.

As a sanity check, we may use Eq. (78) to write the following expression,

$$\langle U \rangle \equiv \left\langle \frac{\kappa q^2}{2} \right\rangle = \frac{\hbar\omega}{4} \coth \frac{\hbar\omega}{2T} \rightarrow \begin{cases} \hbar\omega/4, & \text{at } T \ll \hbar\omega, \\ T/2, & \text{at } \hbar\omega \ll T, \end{cases} \quad (2.79)$$

for the average potential energy of the oscillator. In order to comprehend this result, let us notice that Eq. (72) for the average full energy E was obtained by counting it from the ground state energy $\hbar\omega/2$ of the oscillator.⁴⁶ If we add this energy to the result, we get

Average
energy
including
 $\hbar\omega/2$

$$E = \frac{\hbar\omega}{e^{\hbar\omega/T} - 1} + \frac{\hbar\omega}{2} = \frac{\hbar\omega}{2} \coth \frac{\hbar\omega}{2T}. \quad (2.80)$$

We see that for arbitrary temperature, $\langle U \rangle = E/2$, as we already concluded from Eq. (47). This means that the average kinetic energy, equal to $E - \langle U \rangle$, is also the same:

$$\left\langle \frac{p^2}{2m} \right\rangle = \left\langle \frac{\kappa q^2}{2} \right\rangle = \frac{E}{2} = \frac{\hbar\omega}{4} \coth \frac{\hbar\omega}{2T}. \quad (2.81)$$

In the classical limit $T \gg \hbar\omega$, both energies equal $T/2$, reproducing the equipartition theorem result (48).

2.6. Two important applications

The results of the previous section, especially Eq. (72), have enumerable applications in physics, but I will have time for a brief discussion of only two of them.

⁴⁴ See, e.g., QM Sec. 2.10.

⁴⁵ The calculation may be found, e.g., in QM Sec. 7.2.

⁴⁶ As a quantum mechanics reminder, the ground state energy of the oscillator is not only measurable, but is also responsible for several important phenomena, e.g., the Casimir effect – see, e.g., QM Sec. 9.1.

(i) Blackbody radiation. Let us consider a free-space volume V limited by non-absorbing (i.e. ideally reflecting) walls. Electrodynamics tells us⁴⁷ that electromagnetic field in such a cavity may be presented as a sum of “modes” with time evolution similar to that of the usual harmonic oscillator, and quantum mechanics says⁴⁸ that the energy of such electromagnetic oscillator is quantized in accordance with Eq. (38), so that at thermal equilibrium the average energy is described by Eq. (72). If volume V is large enough,⁴⁹ the number of these modes within a small range dk of the wavevector magnitude k is⁵⁰

$$dN = \frac{gV}{(2\pi)^3} d^3k = \frac{gV}{(2\pi)^3} 4\pi k^2 dk, \quad (2.82)$$

where for electromagnetic waves, the degeneracy factor $g = 2$, due to their two different (e.g., linear) polarizations for the same wave vector $\mathbf{k}$. With the isotropic dispersion relation for waves in vacuum, $k = \omega/c$, the elementary volume d^3k corresponding to a small interval $d\omega$ is a spherical shell of small thickness $dk = d\omega/c$, and Eq. (82) yields

$$dN = \frac{2V}{(2\pi)^3} 4\pi \frac{\omega^2 d\omega}{c^3} = V \frac{\omega^2}{\pi^2 c^3} d\omega. \quad (2.83)$$

Using Eq. (72), we see that the spectral density of electromagnetic wave energy, per unit volume, is

$$u(\omega) \equiv \frac{E}{V} \frac{dN}{d\omega} = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar \omega/T} - 1}. \quad (2.84)$$

Planck's
radiation
law

This is the famous *Planck's blackbody radiation law*.⁵¹ To understand why its name mentions radiation, let us consider a small planar part, of area dA , of a surface that completely absorbs electromagnetic waves incident from any direction. (Such “perfect black body” approximation may be closely approached in special experimental structures, especially in limited frequency intervals.) Figure 8 shows that if the arriving wave was planar, with the incidence angle θ , then power $d\mathcal{P}_\theta(\omega)$ absorbed by the surface within a small frequency interval $d\omega$ (i.e. energy arriving at the surface within unit time interval), would be equal to the radiation energy within the same frequency interval and inside a cylinder of height c , base area $dA \cos \theta$, and hence volume $dV = c dA \cos \theta$:

$$d\mathcal{P}_\theta(\omega) = u(\omega) d\omega dV = u(\omega) d\omega c dA \cos \theta. \quad (2.85)$$

Since the thermally-induced field is isotropic, i.e. propagates equally in all directions, this results should be averaged over all solid angles within the polar angle interval $0 \leq \theta \leq \pi/2$:

$$\frac{d\mathcal{P}(\omega)}{dA d\omega} = \frac{1}{4\pi} \int \frac{d\mathcal{P}_\theta(\omega)}{dA d\omega} d\Omega = cu(\omega) \frac{1}{4\pi} \int_0^{\pi/2} \sin \theta d\theta \int_0^{2\pi} d\phi \cos \theta = \frac{c}{4} u(\omega). \quad (2.86)$$

⁴⁷ See, e.g., EM Sec. 7.9.

⁴⁸ See, e.g., QM Sec. 9.1.

⁴⁹ In our current context, the volume should be much larger than $(c\hbar/T)^3$, where $c \approx 3 \times 10^8$ m/s is the speed of light. For room temperature ($T \approx k_B \times 300\text{K} \approx 4 \times 10^{-21}$ J), that lower bound is of the order of 10^{-16} m³.

⁵⁰ See, e.g., EM Sec. 7.9, or QM Sec. 1.6.

⁵¹ Let me hope the reader knows that the law was first suggested in 1900 by M. Planck as an empirical fit for the experimental data on blackbody radiation, and this was the historic point at which the Planck constant $\hbar$ (or rather $h \equiv 2\pi\hbar$) was introduced - see, e.g., QM Sec. 1.1.

Hence the Planck's formula (84), multiplied by $c/4$, gives the power absorbed by such "blackbody" surface. But at thermal equilibrium, this absorption has to be exactly balanced by the surface's own radiation, due to its finite temperature T .

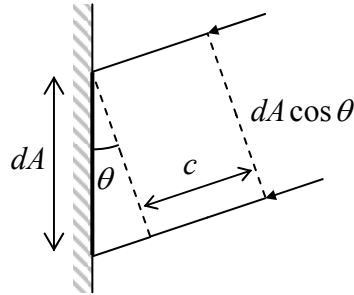


Fig. 2.8. Calculating the relation between $d\mathcal{P}(\omega)$ and $u(\omega)d\omega$.

I am confident that the reader is familiar with the main features of the Planck law (84), including its general shape (Fig. 9), with the low-frequency asymptote $u(\omega) \propto \omega^2$ (due to its historic significance bearing the special name of the *Rayleigh-Jeans law*), the exponential drop at high frequencies (the *Wien law*), and the resulting maximum of function $u(\omega)$, reached at frequency $\omega_{\max}$,

$$\hbar\omega_{\max} \approx 2.28T, \quad (2.87)$$

i.e. at wavelength $\lambda_{\max} = 2\pi/k_{\max} = 2\pi c/\omega_{\max} \approx 2.76 \, c\hbar/T$. Still, I cannot help mentioning two particular values corresponding to visible light ($\lambda_{\max} \sim 500 \, \text{nm}$) for Sun's surface temperature $T_K \approx 6,000 \, \text{K}$, and to mid-infrared range ($\lambda_{\max} \sim 10 \, \mu\text{m}$) for the Earth's surface temperature $T_K \approx 300 \, \text{K}$. The balance of these two radiations, absorbed and emitted by the Earth, determines its surface temperature, and hence has the key importance for all life on our planet. As one more example, the cosmic microwave background (CMB) radiation, closely following the Planck law with $T_K = 2.725 \, \text{K}$ (and hence having maximum density at $\lambda_{\max} \approx 1.9 \, \text{mm}$), and in particular its weak anisotropy, is a major source of data for all modern cosmology.⁵²

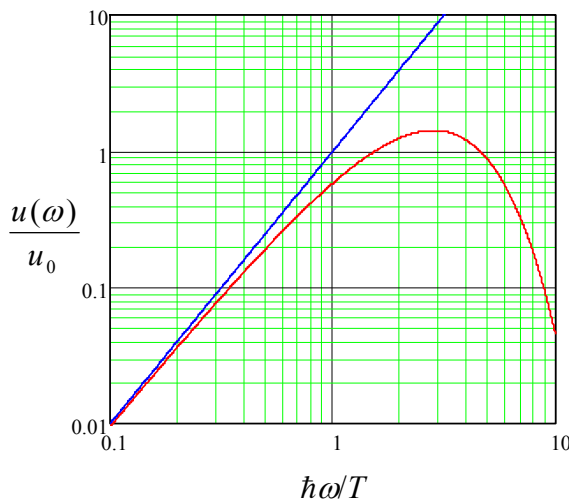


Fig. 2.9. Frequency dependence of the blackbody radiation density, normalized by $u_0 \equiv T^3/\pi^2\hbar^2c^3$, according to the Planck law (red line) and the Rayleigh-Jeans law (blue line).

⁵² For a recent popular book of this topic, see, e.g., S. Singh, *Big Bang: The Origins of the Universe*, HarperCollins, 2005.

Now let us calculate the total energy E of this radiation in some volume V . It may be found from Eq. (72) by integration its over all frequencies:⁵³

$$E = V \int_0^\infty u(\omega) d\omega = V \int_0^\infty \frac{\hbar \omega^3}{\pi^2 c^3} \frac{d\omega}{e^{\hbar \omega/T} - 1} = \frac{VT^4}{\pi^2 \hbar^3 c^3} \int_0^\infty \frac{\xi^3 d\xi}{e^\xi - 1} = V \frac{\pi^2}{15 \hbar^3 c^3} T^4. \quad (2.88)$$

(The last transition in Eq. (88) uses a table integral equal to $\Gamma(4)\zeta(4) = (3!)(\pi^4/90) = \pi^4/15$.⁵⁴) Using Eq. (86) to recast Eq. (88) into the total power radiated by a blackbody surface, we get the well-known *Stefan* (or “Stefan-Boltzmann”) law

$$\frac{d\mathcal{P}}{dA} = \frac{\pi^2}{60 \hbar^3 c^2} T^4 = \sigma T_K^4, \quad (2.89a) \quad \text{Boltzmann law}$$

where σ is the *Stefan-Boltzmann constant*

$$\sigma \equiv \frac{\pi^2}{60 \hbar^3 c^2} k_B^4 \approx 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}. \quad (2.89b) \quad \text{Stephan-Boltzmann constant}$$

By this time, the thoughtful reader should have an important concern ready: Eq. (84) and hence Eq. (88) are based on Eq. (72) for the average energy of each oscillator, counted from its ground energy $\hbar\omega/2$. However, the radiation power should not depend on the energy origin; why have not we included the ground energy of each oscillator into integration (88), as we have done in Eq. (80)? The answer is that usual radiation detectors only measure the *difference* between power $\mathcal{P}_{\text{in}}$ of the incident radiation (say, that of a blackbody surface with temperature T) and their own back-radiation $\mathcal{P}_{\text{out}}$ with power corresponding to some effective temperature T_d of the detector (Fig. 10). But however low T_d is, the temperature-independent ground state energy contribution $\hbar\omega/2$ to the back radiation is always there. Hence, the $\hbar\omega/2$ drops out from the difference, and cannot be detected - at least in this simple way. This is the reason why we had the right to ignore this contribution in Eq. (88) – very fortunately, because it would lead to the integral’s divergence at its upper limit. However, let me repeat again that the ground-state energy of the electromagnetic field oscillators is physically real – and important.

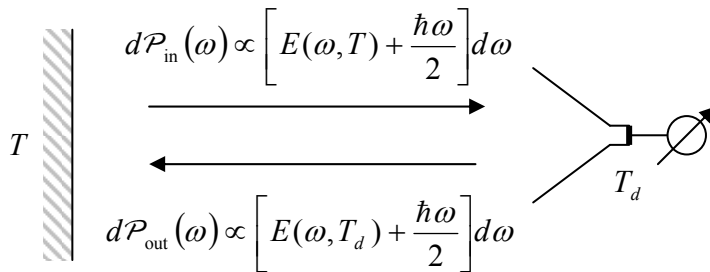


Fig. 2.10. Generic scheme of the electromagnetic radiation power measurement.

⁵³ Note that the heat capacity $C_V \equiv (\partial E / \partial T)_V$, following from Eq. (88), is proportional to T^3 at any temperature, and hence does not obey the trend $C_V \rightarrow \text{const}$ at $T \rightarrow \infty$. This is the result of the unlimited growth, with temperature, of the number of thermally-excited field oscillators with $\hbar\omega < T$.

⁵⁴ See, e.g., MA Eqs. (6.8b), (6.6b), and (2.7b).

One more interesting result may be deduced from the free energy F of the electromagnetic radiation, which may be also calculated by integration of Eq. (73) over all the modes, with the appropriate weight:

$$F = \sum_{\omega} T \ln(1 - e^{-\hbar\omega/T}) \rightarrow \int_0^{\infty} T \ln(1 - e^{-\hbar\omega/T}) \frac{dN}{d\omega} d\omega = \int_0^{\infty} T \ln(1 - e^{-\hbar\omega/T}) \left(V \frac{\omega^2}{\pi^2 c^3} \right) d\omega. \quad (2.90)$$

Presenting $\omega^2 d\omega$ as $d(\omega^3)/3$, this integral may be readily worked out by parts, and reduced to a table integral similar to that in Eq. (88), yielding a surprisingly simple result:

$$F = -V \frac{\pi^2}{45 \hbar^3 c^3} T^4 = -\frac{E}{3}. \quad (2.91)$$

Now we can use the second of general thermodynamic equations (1.35) to calculate pressure:

$$P = -\left(\frac{\partial F}{\partial V} \right)_T = \frac{\pi^2}{45 \hbar^3 c^3} T^4 = \frac{E}{3V}. \quad (2.92a)$$

This result might be, of course, derived by the integration of the expression for the forces exerted by each mode of the electromagnetic on confining the walls confining it to volume V ,⁵⁵ but notice how much simpler the thermodynamic calculation is. Rewritten in the form,

Photon
gas'
equation of
state

$$PV = \frac{E}{3}, \quad (2.92b)$$

this result may be considered as the equation of state of the electromagnetic field, i.e. from the quantum-mechanical point of view, the *photon gas*. As we will prove in the next chapter, the equation of state (1.44) of the ideal classical gas may be presented in a similar form, but with a coefficient generally different from Eq. (92). In particular, according to the equipartition theorem, for an ideal gas of nonrelativistic atoms whose internal degrees of freedom are in their ground state, whose whole energy is that of three translational “half-degrees of freedom”, $E = 3N(T/2)$, the factor before E is twice larger than in Eq. (92). On the other hand, a *relativistic* treatment of the classical gas shows that Eq. (92) is valid for any gas in the ultrarelativistic limit, $T \gg mc^2$, where m is the rest mass of the gas particle. Evidently, photons (i.e. particles with $m = 0$) satisfy this condition.⁵⁶

Finally, let me note that Eq. (92) allows the following interesting interpretation. The last of Eqs. (1.60), being applied to Eq. (92), shows that in this particular case the grand potential Ω equals $(-E/3)$. But according to the definition of Ω , the first of Eqs. (1.60), this means that the chemical potential of the electromagnetic field excitations vanishes:

$$\mu = \frac{F - \Omega}{N} = 0. \quad (2.93)$$

In Sec. 8 below, we will see that the same result follows from Eq. (72) and the Bose-Einstein distribution, and discuss its physical sense.

⁵⁵ See, e.g., EM Sec. 9.8.

⁵⁶ Please note that according to Eqs. (1.44), (88), and (92), the difference between the equations of state of the photon gas and an ideal gas of nonrelativistic particles, expressed in the more usual form - as $P = P(V, T)$, is much more dramatic: $P \propto T^4 V^0$ instead of $P \propto T^1 V^{-1}$.

(ii) Specific heat of solids. The heat capacity of solids is readily measurable, and in the early 1900s its experimentally observed temperature dependence served as an important test for emerging quantum theories. However, theoretical calculation of C_V is not simple,⁵⁷ even for isolators whose specific heat is due to thermally-induced vibrations of their crystal lattice alone.⁵⁸ Indeed, a solid may be treated as an elastic continuum only at low relatively frequencies. Such continuum supports three different modes of mechanical waves with the same frequency ω , that obey similar, linear dispersion laws, $\omega = vk$, but velocity $v = v_l$ for one of these modes (the *longitudinal sound*) is higher than that (v_t) of two other modes (the *transverse sound*).⁵⁹ At such frequencies the wave mode density may be described by an evident modification of Eq. (83):

$$dN = V \frac{1}{(2\pi)^3} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) 4\pi\omega^2 d\omega. \quad (2.94a)$$

For what follows, it is convenient to rewrite this relation in a form similar to Eq. (83):

$$dN = \frac{3V}{(2\pi)^3} 4\pi \frac{\omega^2 d\omega}{v^3}, \quad \text{with } v \equiv \left[\frac{1}{3} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \right]^{-1/3}. \quad (2.94b)$$

However, wave theory shows⁶⁰ that as frequency ω of a sound wave in a periodic structure is increased so that its half-wavelength π/k approaches the crystal period d , the dispersion law $\omega(k)$ becomes nonlinear before the frequency reaches a maximum at $k = \pi/d$. To make the things even more complex, 3D crystals are generally anisotropic, so that the dispersion law is different in different directions of wave propagation. As a result, the exact statistics of thermally excited sound waves, and hence the heat capacity of crystals, is rather complex and specific for each particular crystal type.

In 1912, P. Debye suggested an approximate theory of the temperature dependence of the specific heat, which is in a surprisingly good agreement with experiment for many insulators, including polycrystalline and amorphous materials. In his model, the linear (*acoustic*) dispersion law $\omega = vk$, with the effective sound velocity v , defined by the latter of Eqs. (94b), is assumed to be exact all the way up to some cutoff frequency ω_D , the same for all three wave modes. This cutoff frequency may be defined by the requirement that the total number of acoustic modes, calculated within this model from Eq. (94b),

$$N = V \frac{1}{(2\pi)^3} \frac{3}{v^3} \int_0^{\omega_D} 4\pi\omega^2 d\omega = \frac{V\omega_D^3}{2\pi^2 v^3}, \quad (2.95)$$

is equal to the universal number $N = 3nV$ of degrees of freedom (and hence of independent oscillation modes) in a system of nV elastically coupled particles, where n is the atomic density of the crystal, i.e. the number of atoms per unit volume. Within this model, Eq. (72) immediately yields the following expression for the average energy and specific heat (in thermal equilibrium at temperature T):

⁵⁷ Due to low temperature expansion of solids, the difference between their C_V and C_P is small.

⁵⁸ In good conductors (e.g., metals), specific heat is contributed (and at low temperatures, dominated) by free electrons – see Sec. 3.3 below.

⁵⁹ See, e.g., CM Sec. 7.7.

⁶⁰ See, e.g., CM Sec. 5.3, in particular Fig. 5.5 and its discussion.

$$E = V \frac{1}{(2\pi)^3} \frac{3}{v^3} \int_0^{\omega_D} \frac{\hbar\omega}{e^{\hbar\omega/T} - 1} 4\pi\omega^2 d\omega = 3nVT \cdot D(x)_{x=T_D/T}, \quad (2.96)$$

Debye
law

$$c_V \equiv \frac{C_V}{nV} = \frac{1}{nV} \left(\frac{\partial E}{\partial T} \right)_V = 3 \left[D(x) - x \frac{dD(x)}{dx} \right]_{x=T_D/T}, \quad (2.97)$$

where $T_D \equiv \hbar\omega_D$ is called the *Debye temperature*,⁶¹ and

$$D(x) \equiv \frac{3}{x^3} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} \rightarrow \begin{cases} 1, & \text{at } x \rightarrow 0, \\ \pi^4/5x^3, & \text{at } x \rightarrow \infty, \end{cases} \quad (2.98)$$

the *Debye function*. Red lines in Fig. 11 show the temperature dependence of the specific heat c_V (per atom) within the Debye model. At high temperatures, it approaches a constant value of 3, corresponding to energy $E = 3nVT$, in accordance with the equipartition theorem for each of 3 degrees of freedom of each atom. (This model-insensitive value of c_V is known as the *Dulong-Petit law*.) In the opposite limit of low temperatures, the specific heat is much smaller:

$$c_V \approx \frac{12\pi^4}{5} \left(\frac{T}{T_D} \right)^3 \ll 1, \quad (2.99)$$

reflecting the reduction of the number of excited waves with $\hbar\omega < T$ as the temperature is decreased.

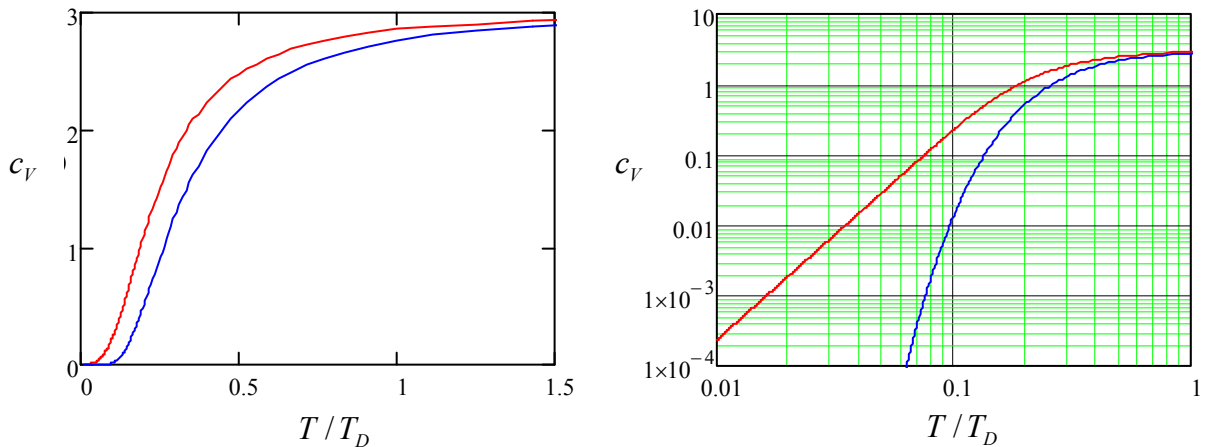


Fig. 2.11. Temperature dependence of the specific heat in the Debye (red lines) and Einstein (blue lines) models.

As a historic curiosity, P. Debye's work followed one by A. Einstein, who had suggested (in 1907) a simpler model of crystal vibrations. In this model, all $3nV$ independent oscillatory modes of nV atoms of the crystal have approximately the same frequency, say ω_E , and Eq. (72) immediately yields

⁶¹ In SI units, Debye temperatures T_D are of the order of a few hundred K for most simple solids (e.g., close to 430 K for aluminum and 340 K for copper), with somewhat lower values for crystals with heavy atoms (~ 105 K for lead), and reach the highest value ~ 2200 K for diamond with its relatively light atoms and very stiff lattice.

$$E = 3nV \frac{\hbar\omega_E}{e^{\hbar\omega_E/T} - 1}, \quad (2.100)$$

so that the specific heat is functionally similar to Eq. (75):

$$c_V \equiv \frac{1}{nV} \left(\frac{\partial E}{\partial T} \right)_V = 3 \left[\frac{\hbar\omega_E / 2T}{\sinh(\hbar\omega_E / 2T)} \right]^2. \quad (2.101)$$

This dependence $c_V(T)$ is shown with blue lines in Fig. 11 (assuming, for the sake of simplicity, $\hbar\omega_E = T_D$). At high temperatures, this result does satisfy the universal Dulong-Petit law ($c_V = 3$), but at low temperatures the Einstein's model predicts a much faster (exponential) drop of the specific heat as the temperature is reduced. (The difference between the Debye and Einstein models is not too spectacular on the linear scale, but in the log-log plot, shown on the right panel of Fig. 11, it is rather dramatic.⁶²) The Debye model is in a much better agreement with experimental data for simple, monoatomic crystals, thus confirming the conceptual correctness of his wave-based approach.

Note, however, that when a genius such as A. Einstein makes an error, there is probably some deep and important reason behind it. Indeed, crystals with the basic cell consisting of atoms of two or more types (such as NaCl, etc.), feature two or more separate branches of the dispersion law $\omega(k)$ – see, e.g., Fig. 12.⁶³

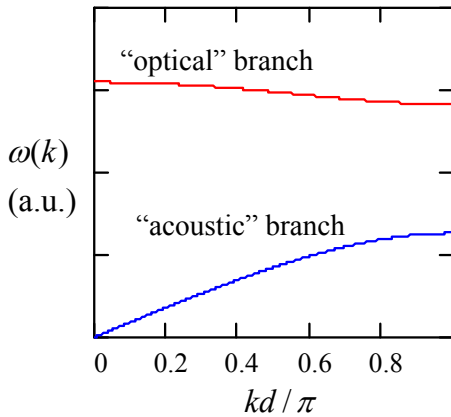


Fig. 2.12. Dispersion relation for longitudinal waves in a simple 1D model of a solid, with similar interparticle distances d , but alternating particle masses, plotted for a particular mass ratio $r = 5$.

While the lower “acoustic” branch is virtually similar to those for monoatomic crystals, and may be approximated by the Debye model, $\omega = vk$, reasonably well, the upper (“optical”⁶⁴) branch does approach $\omega = 0$ at any k . Moreover, for large values of the atom mass ratio r , the optical branches are almost flat, with virtually k -independent frequencies ω_0 that correspond to simple oscillations of each light atom between its heavy counterparts. For thermal excitations of such oscillations, and their

⁶² This is why there is a general “rule of thumb” in science: if you plot your data on a linear rather than log scale, you better have a good excuse ready. (A valid excuse example: the variable you are plotting changes sign within the important range.)

⁶³ This is the exact solution of a particular 1D model of such a crystal – see CM Chapter 5.

⁶⁴ This term stems from the fact that at $k \rightarrow 0$, the mechanical waves corresponding to these branches have phase velocities $v_{ph} \equiv \omega(k)/k$ that are much higher than that of the acoustic waves, and may approach the speed of light. As a result, these waves can strongly interact with electromagnetic (practically, optical) waves of the same frequency, while the acoustic waves cannot.

contribution to the specific heat, the Einstein model (with $\omega_E = \omega_0$) gives a very good approximation, so that the specific heat may be well described by a sum of the Debye and Einstein laws (97) and (101), with appropriate weights.

2.7. Grand canonical ensemble and distribution

As we have seen, the Gibbs distribution is a very convenient way to calculate statistical and thermodynamic properties of systems with a fixed number N of particles. However, for systems in which N may vary, another distribution is preferable for some applications. Several examples of such situations (as well as the basic thermodynamics of such systems) have already been discussed in Sec. 1.5. Perhaps even more importantly, statistical distributions for systems with variable N are also applicable to the ensembles of independent particles on a certain single-particle energy level – see the next section.

With this motivation, let us consider what is called the *grand canonical ensemble* (Fig. 13). It is similar to the canonical ensemble discussed in the previous section (Fig. 6) in all aspects, besides that now the system under study and the heat bath (in this case typically called the *environment*) may exchange not only heat but also particles. In all system members of the ensemble, the environments are in both the thermal and chemical equilibrium, and their temperatures T and chemical potentials μ are equal.

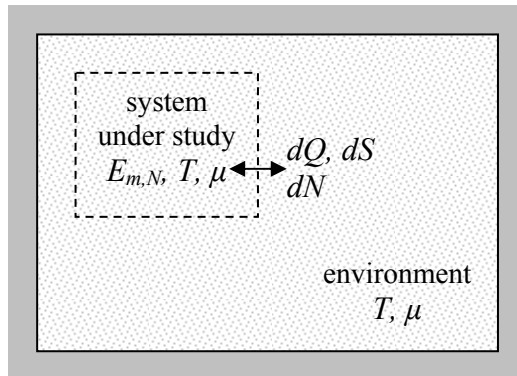


Fig. 2.13. Member of a grand canonical ensemble.

Now let us assume that the system of interest is also in the chemical and thermal equilibrium with its environment. Then using exactly the same arguments as in Sec. 4 (including the specification of a microcanonical sub-ensemble with fixed E_Σ and N_Σ), we may generalize Eq. (55), taking into account that entropy S_{env} of the environment is now a function of not only its energy $E_{\text{env}} = E_\Sigma - E_{m,N}$,⁶⁵ but also the number of particles $N_E = N_\Sigma - N$, with E_Σ and N_Σ fixed:

$$\begin{aligned} \ln W_{m,N} &\propto \ln M = \ln g_{\text{env}}(E_\Sigma - E_{m,N}, N_\Sigma - N) + \ln \Delta E_\Sigma = S_{\text{env}}(E_\Sigma - E_{m,N}, N_\Sigma - N) + \text{const} \\ &\approx S_{\text{env}} \Big|_{E_\Sigma, N_\Sigma} - \frac{\partial S_{\text{env}}}{\partial E_{\text{env}}} \Big|_{E_\Sigma, N_\Sigma} E_{m,N} - \frac{\partial S_{\text{env}}}{\partial N_{\text{env}}} \Big|_{E_\Sigma, N_\Sigma} N + \text{const}. \end{aligned} \quad (2.102)$$

In order to simplify this relation, we may rewrite Eq. (1.52) in the equivalent form

⁶⁵ The additional index in the new notation $E_{m,N}$ for the energy of the system of interest reflects the fact that its eigenvalue spectrum is generally dependent on the number N of particles in it.

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN. \quad (2.103)$$

Hence, if entropy S of a system is expressed as a function of E , V , and N , then

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}, \quad \left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}. \quad (2.104)$$

Applying the first one and the last one of these relations to Eq. (102), and using the equality, of the temperatures T and chemical potentials μ of the system under study and its environment, at their equilibrium, discussed in Sec. 1.5, we get

$$\ln W_{m,N} = S_{\text{env}}(E_{\Sigma}, N_{\Sigma}) - \frac{1}{T} E_{m,N} + \frac{\mu}{T} N + \text{const}. \quad (2.105)$$

Again, exactly as at the derivation of the Gibbs distribution in Sec. 4, we may argue that since $E_{m,N}$, T and μ do not depend on the choice of environment's size, i.e. on E_{Σ} and N_{Σ} , the probability $W_{m,N}$ for a system to have N particles and be in m -th quantum state in the whole grand canonical ensemble should also obey a relation similar to Eq. (105). As a result, we get the so-called *grand canonical distribution*:

$$W_{m,N} = \frac{1}{Z_G} \exp\left\{\frac{\mu N - E_{m,N}}{T}\right\}. \quad (2.106)$$

Grand
canonical
distribution

Just as in the case of the Gibbs distribution, constant Z_G (most often called the *grand statistical sum*, but sometimes the “grand partition function”) should be determined from the probability normalization condition, now with the summation of probabilities $W_{m,N}$ over all possible values of both m and N :

$$Z_G = \sum_{m,N} \exp\left\{\frac{\mu N - E_{m,N}}{T}\right\}. \quad (2.107)$$

Grand
canonical
sum

Now, using the general Eq. (29) to calculate entropy for distribution (106) (exactly like we did it for the canonical ensemble), we get the following expression,

$$S = -\sum_{m,N} W_{m,N} \ln W_{m,N} = \ln Z_G + \frac{E}{T} - \frac{\mu \langle N \rangle}{T}, \quad (2.108)$$

which is evidently a generalization of Eq. (62).⁶⁶ We see that now the grand thermodynamic potential Ω (rather than the free energy F) may be expressed directly via the normalization coefficient Z_G :

$$\Omega \equiv F - \mu \langle N \rangle = E - TS - \mu \langle N \rangle = T \ln \frac{1}{Z_G} = -T \ln \sum_{m,N} \exp\left\{\frac{\mu N - E_{m,N}}{T}\right\}. \quad (2.109)$$

Ω from Z_G

Finally, solving the last equality for Z_G , and plugging the result back into Eq. (106), we can rewrite the grand canonical distribution in the form

⁶⁶ The average number of particles $\langle N \rangle$ is of course exactly what was called N in thermodynamics (see Ch. 1), but I need to keep this explicit notation here to make a clear distinction between this average value of the variable, and its particular values participating in Eqs. (102)-(110).

$$W_{m,N} = \exp\left\{\frac{\Omega + \mu N - E_{m,N}}{T}\right\}, \quad (2.110)$$

similar to Eq. (65) for the Gibbs distribution. Indeed, in the particular case when the number N of particles is fixed, $N = \langle N \rangle$, so that $\Omega + \mu N = \Omega + \mu \langle N \rangle \equiv F$, Eq. (110) is reduced right to Eq. (65).

2.8. Systems of independent particles

Now we will use the general statistical distributions discussed above to a simple but very important case when each system we are considering consists of many similar particles whose explicit (physical) interaction is negligible. As a result, each particular energy value $E_{m,N}$ of such a system may be presented as a sum of energies ε_k of its particles, where index k numbers single-particle energy levels (rather than of the whole system, as index m does).

Let us start with the classical limit. In classical mechanics, the quantization effects are negligible, i.e. there is a virtually infinite number of states k within each finite energy interval. However, it is convenient to keep, for the time being, the discrete-state language, with understanding that the average number $\langle N_k \rangle$ of particles in each of these states, frequently called the *state occupancy*, is very small. In this case, we may apply the Gibbs distribution to the canonical ensemble of *single particles*, and hence use it with the substitution $E_{m,N} \rightarrow \varepsilon_k$, so that Eq. (58) becomes

Boltzmann
distribution

$$\langle N_k \rangle = c \exp\left\{-\frac{\varepsilon_k}{T}\right\} \ll 1, \quad (2.111)$$

where constant c should be found from the normalization condition:

$$\sum_k \langle N_k \rangle = 1. \quad (2.112)$$

This is the famous *Boltzmann distribution*.⁶⁷ Despite its superficial similarity to the Gibbs distribution (58), let me emphasize the conceptual difference between these two results. The Gibbs distribution describes the probability to find the *whole system* on energy level E_m , and it is *always* valid - more exactly, for a canonical ensemble of systems in thermodynamic equilibrium. On the other hand, the Boltzmann distribution describes occupancy of an energy level of a *single particle*, and for systems of identical particles is valid *only in the classical limit* $\langle N_k \rangle \ll 1$, even if the particles do not interact directly.

The last fact may be surprising, because it may seem that as soon as particles of the system are independent, nothing prevents us from using the Gibbs distribution to derive Eq. (111), regardless of the value of $\langle N_k \rangle$. This is indeed true if the particles are *distinguishable*, i.e. may be distinguished from each other - say by their fixed spatial positions, or by the states of certain internal degrees of freedom (say, spin), or any other “pencil mark”. However, it is an experimental fact that elementary particles of each particular type (say, electrons) are *identical* to each other, i.e. cannot be “pencil-marked”. For such particles we have to be more careful: even if they do not interact *explicitly*, there is still some *implicit*

⁶⁷ The distribution was first suggested in 1877 by the founding father of statistical physics, L. Boltzmann. For the particular case when ε is the kinetic energy of a free classical particle (and hence has a continuous spectrum), it is reduced to the *Maxwell distribution* – see Sec. 3.1 below.

dependence in their behavior, which is especially evident for the so-called *fermions* (fundamental particles with semi-integer spin) they obey the *Pauli exclusion principle* that forbids two identical particles to be in the same quantum state, even if they do not interact explicitly.⁶⁸

Note that here the term “the same quantum state” carries a heavy meaning load here. For example, if two particles are confined to stay in different spatial positions (say, reliably locked in different boxes), they are *distinguishable* even if they are internally identical. Thus the Pauli principle, as well as other identity effects such as Bose-Einstein condensation, to be discussed in the next chapter, are important only when identical particles may move in the same spatial region. In order to describe this case, instead of “identical”, it is much better to use a more precise (though ugly) term *indistinguishable* particles.⁶⁹

In order to take these effects into account, let us examine the effects of nonvanishing occupancy $\langle N_k \rangle \sim 1$ on statistical properties of a system of many non-interacting but indistinguishable particles (at the first stage of calculation, either fermions or bosons) in equilibrium, and apply the grand canonical distribution (109) to a very interesting particular grand canonical ensemble: a subset of particles in the same quantum state k (Fig. 14).

single-particle energy levels:

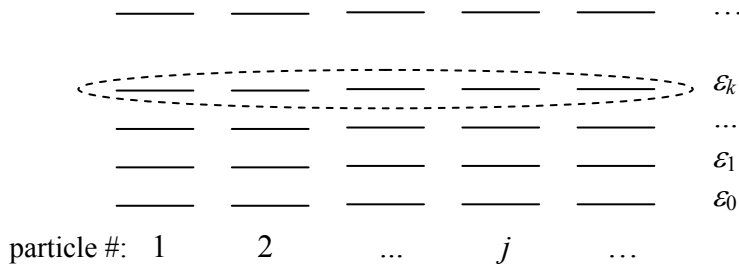


Fig. 2.14. Grand canonical ensemble of particles in the same quantum state (with eigenenergy ε_k).

In this ensemble, the role of the environment is played by the particles in all other states $k' \neq k$, because due to infinitesimal interactions, the particles may change their states. In equilibrium, the chemical potential μ and temperature T of the system should not depend on the state number k , but the grand thermodynamic potential Ω_k of the chosen particle subset may. Replacing N with N_k - the particular (not average!) number of particles in k^{th} state, and the particular energy value $E_{m,N}$ with $\varepsilon_k N_k$, we may reduce Eq. (109) to

$$\Omega_k = -T \ln \left(\sum_{N_k} \exp \left\{ \frac{\mu N_k - \varepsilon_k N_k}{T} \right\} \right) = -T \ln \left[\sum_{N_k} \left(\exp \left\{ \frac{\mu - \varepsilon_k}{T} \right\} \right)^{N_k} \right], \quad (2.113)$$

⁶⁸ See, e.g., QM Sec. 8.1.

⁶⁹ This invites a natural question: what particles are “elementary enough” for the identity? For example, protons and neutrons have an internal structure, in some sense consisting of quarks and gluons; they be considered elementary? Next, if protons and neutrons are elementary, are atoms? molecules? What about *really* large molecules (such as proteins)? viruses? The general answer to these questions, given by quantum mechanics (or rather experiment :-), is that any particles/systems, no matter how large and complex they are, are identical if they have exactly the same internal structure, and also are exactly in the same internal quantum state – for example, in the ground state of all their internal degrees of freedom.

where the summation should be carried out over all possible values of N_k . For the final calculation of this sum, the elementary particle type becomes essential.

In particular, for *fermions*, obeying the Pauli principle, numbers N_k in Eq. (113) may take only two values, either 0 (state k is unoccupied) or 1 (the state is occupied), and the summation gives

$$\Omega_k = -T \ln \left[\sum_{N_k=0,1} \left(\exp \left\{ \frac{\mu - \varepsilon_k}{T} \right\} \right)^{N_k} \right] = -T \ln \left(1 + \exp \left\{ \frac{\mu - \varepsilon_k}{T} \right\} \right). \quad (2.114)$$

Now the average occupancy may be calculated from the last of Eqs. (1.62) – in this case, with N replaced with $\langle N_k \rangle$:

Fermi-
Dirac
distribution

$$\langle N_k \rangle = - \left(\frac{\partial \Omega_k}{\partial \mu} \right)_{T,V} = \frac{1}{e^{(\varepsilon_k - \mu)/T} + 1}. \quad (2.115)$$

This is the famous *Fermi-Dirac distribution*, derived in 1926 independently by E. Fermi and P. Dirac.

On the other hand, *bosons* do *not* obey the Pauli principle, and for them numbers N_k can take any non-negative integer values. In this case, Eq. (113) turns into the following equality:

$$\Omega_k = -T \ln \sum_{N_k=0}^{\infty} \left(\exp \left\{ \frac{\mu - \varepsilon_k}{T} \right\} \right)^{N_k} = -T \ln \sum_{N_k=0}^{\infty} \lambda^{N_k}, \quad \text{with } \lambda \equiv \exp \left\{ \frac{\mu - \varepsilon_k}{T} \right\}. \quad (2.116)$$

This sum is just the usual geometric progression again, which converges if $\lambda < 1$, giving

$$\Omega_k = -T \ln \frac{1}{1 - \lambda} = -T \ln \frac{1}{1 - e^{(\mu - \varepsilon_k)/T}}, \quad \text{for } \mu < \varepsilon_k. \quad (2.117)$$

In this case the average occupancy, again calculated using Eq. (1.62) with N replaced with $\langle N_k \rangle$, obeys the *Bose-Einstein distribution*,

Bose-
Einstein
distribution

$$\langle N_k \rangle = - \left(\frac{\partial \Omega_k}{\partial \mu} \right)_{T,V} = \frac{1}{e^{(\varepsilon_k - \mu)/T} - 1}, \quad \text{for } \mu < \varepsilon_k, \quad (2.118)$$

which was derived in 1924 by S. Bose (for the particular case $\mu = 0$) and generalized in 1925 by A. Einstein for an arbitrary chemical potential. In particular, comparing Eq. (118) with Eq. (72), we see that harmonic oscillator *excitations*,⁷⁰ each with energy $\hbar\omega$, may be considered as bosons, with zero chemical potential. We have already obtained this result ($\mu = 0$) in a different way – see Eq. (93). Its physical interpretation is that the oscillator excitations may be created inside the system, so that there is no energy cost μ of moving them into the system from its environment.

The simple form of Eqs. (115) and (118), and their similarity (besides “only” the difference of the signs before unity in their denominators), is one of most beautiful results of physics. This similarity should not disguise the facts that the energy dependences of $\langle N_k \rangle$, given by these two formulas, are rather different – see Fig. 15. In the Fermi-Dirac statistics, the average level occupancy is finite (and

⁷⁰ As the reader certainly knows, for the electromagnetic field oscillators, such excitations are called *photons*; for mechanical oscillation modes, *phonons*. It is important, however, not to confuse these mode *excitations* with the oscillators as such, and be very careful in prescribing to them certain spatial locations – see, e.g., QM Sec. 9.1.

below 1) at any energy, while in the Bose-Einstein it may be above 1, and even diverges at $\varepsilon_k \rightarrow \mu$. However, for any of these distributions, as temperature is increased, it eventually becomes much larger than the difference $(\varepsilon_k - \mu)$ for all k . In this limit, $\langle N_k \rangle \ll 1$, both distributions coincide with each other, as well as with the Boltzmann distribution (111) with $c = \exp\{\mu/T\}$. The last distribution, therefore, serves as the high-temperature limit for quantum particles of both sorts.

A natural question now is how to find the chemical potential μ participating in Eqs. (115) and (118). In the grand canonical ensemble as such (Fig. 13), with number of particles variable, the value of μ is imposed by system's environment. However, both the Fermi-Dirac and Bose-Einstein distributions are also applicable to equilibrium systems with a *fixed but large* number N of particles. In these conditions, the role of the environment for some subset of $N' \ll N$ particles is played by the remaining $N - N'$ particles. In this case, μ may be found by calculation of $\langle N \rangle$ from the corresponding distribution, and then requiring it to be equal to the genuine number of particles in the system. In the next section, we will perform such calculations for several particular systems.

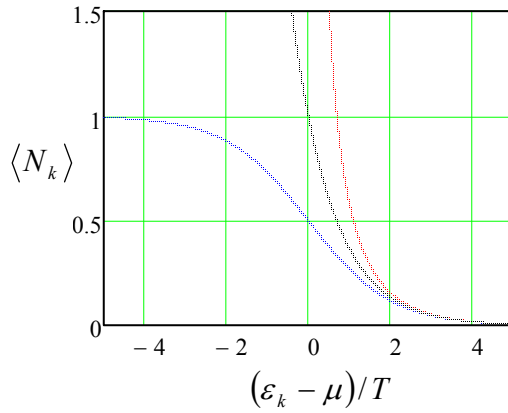


Fig. 2.15. Fermi-Dirac (blue line) and Bose-Einstein (red line) distributions, and the Boltzmann distribution with $c = \exp\{\mu/T\}$ (black line).

For those and other applications, it will be convenient for us to have ready expressions for entropy S of a general (i.e. not necessarily equilibrium) state of systems of independent Fermi or Bose particles, expressed not as a function of W_m of the whole system – as Eq. (29) does, but as a function of the average occupancy numbers $\langle N_k \rangle$. For that, let us consider a *composite system*, each consisting of $M \gg 1$ similar but distinct *component systems*, numbered by index $m = 1, 2, \dots, M$, with independent (i.e. not *explicitly* interacting) particles. We will assume that though in each of M component systems, the number $N_k^{(m)}$ of particles in its k -th quantum state may be different (Fig. 16), but their total number $N_k^{(\Sigma)}$ in the composite system is fixed:

$$\sum_{m=1}^M N_k^{(m)} = N_k^{(\Sigma)}. \quad (2.119)$$

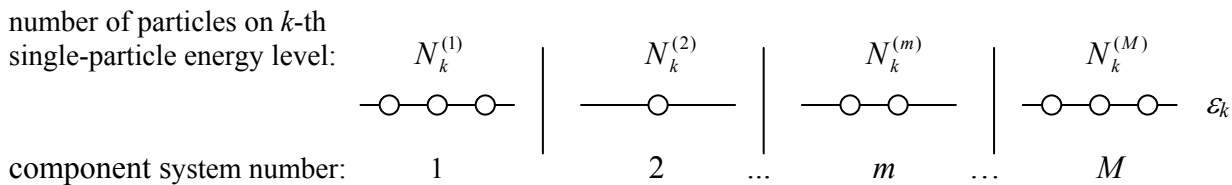


Fig. 2.16. Composite system with a certain distribution of $N_k^{(\Sigma)}$ particles in k -th state between M component systems.

As a result, the total energy of the composite system is fixed as well,

$$\sum_{m=1}^M N_k^{(m)} \varepsilon_k = N_k^{(\Sigma)} \varepsilon_k = \text{const}, \quad (2.120)$$

so that an ensemble of many such composite systems (with the same k), in equilibrium, is microcanonical. According to Eq. (24a), the average entropy S_k per component system may be calculated as

$$S_k = \lim_{M, N_k \rightarrow \infty} \frac{\ln M_k}{M}, \quad (2.121)$$

where M_k is the number of possible different ways such composite system (with fixed $N_k^{(\Sigma)}$) may be implemented.

Let us start the calculation of M_k with Fermi particles - for which the Pauli principle is valid. Here the level occupancies $N_k^{(m)}$ may be only equal 0 or 1, so that the distribution problem is solvable only if $N_k^{(\Sigma)} \leq M$, and evidently equivalent to the choice of $N_k^{(\Sigma)}$ balls (in *arbitrary* order) from the total number of M *distinct* balls. Comparing this formulation with the binomial coefficient definition,⁷¹ we immediately have

$$M_k = {}^M C_{N_k^{(\Sigma)}} = \frac{M!}{(M - N_k^{(\Sigma)})! N_k^{(\Sigma)}!}. \quad (2.122)$$

From here, using the Stirling formula (again, in its simplest form (27)), we get

Fermion
entropy

$$S_k = -\langle N_k \rangle \ln \langle N_k \rangle - (1 - \langle N_k \rangle) \ln (1 - \langle N_k \rangle), \quad (2.123)$$

where

$$\langle N_k \rangle \equiv \lim_{M, N_k \rightarrow \infty} \frac{N_k^{(\Sigma)}}{M} \quad (2.124)$$

is exactly the average occupancy of the k -th single-particle level in each system that was discussed earlier in this section. Since for a Fermi system, $\langle N_k \rangle$ is always somewhere between 0 and 1, so that entropy (123) is always positive.

In the Bose case, where the Pauli limitation is not valid, the number $N_k^{(m)}$ of particles on the k -th level in each of the systems is an arbitrary (positive) integer. Let us consider $N_k^{(\Sigma)}$ particles and $(M - 1)$ partitions (shown by vertical lines in Fig. 16) between M systems as $(M - 1 + N_k^{(\Sigma)})$ similar mathematical objects ordered along one axis. Then M_k may be calculated as the number of possible ways to distribute the $(M - 1)$ indistinguishable partitions among these $(M - 1 + N_k^{(\Sigma)})$ distinct objects, i.e. as the following binomial coefficient:⁷²

$$M_k = {}^{M+N_k-1} C_{M-1} = \frac{(M - 1 + N_k^{(\Sigma)})!}{(M - 1)! N_k^{(\Sigma)}!}. \quad (2.125)$$

⁷¹ See, e.g., MA Eq. (2.2).

⁷² See also MA Eq. (2.4).

Applying the Stirling formula (27) again, we get the following result,

$$S_k = -\langle N_k \rangle \ln \langle N_k \rangle + (1 + \langle N_k \rangle) \ln(1 + \langle N_k \rangle), \quad (2.126) \quad \text{Boson entropy}$$

which again differs from the Fermi case (123) “only” by the signs in the second term, and is valid for any positive $\langle N_k \rangle$.

Expressions (123) and (126) are valid for an arbitrary (possibly non-equilibrium) case; they may be also used for an alternative derivation of the Fermi-Dirac (115) and Bose-Einstein (118) distributions valid in equilibrium. For that, we may use the method of Lagrange multipliers, requiring (just like it was done in Sec. 2) the total entropy of a system of N independent, similar particles,

$$S = \sum_k S_k, \quad (2.127)$$

as a function of state occupancies $\langle N_k \rangle$, to attain its maximum, with the conditions of fixed total number of particles N and the total energy E :

$$\sum_k \langle N_k \rangle = N = \text{const}, \quad \sum_k \langle N_k \rangle \varepsilon_k = E = \text{const}. \quad (2.128)$$

The completion of this calculation is left for reader's exercise.

In the classical limit, when the average occupancies $\langle N_k \rangle$ of all states are small, both the Fermi and Bose expressions for S_k tend to the same limit

$$S_k = -\langle N_k \rangle \ln \langle N_k \rangle, \quad \text{for } \langle N_k \rangle \ll 1. \quad (2.129) \quad \text{Boltzmann entropy}$$

This expression, frequently referred to as the *Boltzmann* (or “classical”) *entropy*, might be also obtained, for arbitrary $\langle N_k \rangle$, directly from Eq. (29) by considering an ensemble of systems, each consisting of just one classical particle, so that $E_m \rightarrow \varepsilon_k$ and $W_m \rightarrow \langle N_k \rangle$. Let me emphasize again that for indistinguishable particles, such identification is generally (i.e. at $\langle N_k \rangle \sim 1$) illegitimate even if they do not interact explicitly. As we will see in the next chapter, the indistinguishability affects statistical properties of even classical particles.

2.9. Exercise problems

2.1. A famous example of the macroscopic irreversibility was suggested in 1907 by P. Ehrenfest. Two dogs share $2N \gg 1$ fleas. Each flea may jump to another dog, and the rate (i.e. the probability of jumping per unit time) Γ of such an event does not depend on time, and on the location of other fleas. Find the time evolution of the average number of fleas on a dog, and of the flea-related part of dogs' entropy (at arbitrary initial conditions), and prove that the entropy can only grow.⁷³

2.2. Use the microcanonical distribution to calculate thermodynamic properties (including entropy, all relevant thermodynamic potentials, and heat capacity), of an ensemble of similar two-level

⁷³ This is essentially a simpler (and funnier :-)) version of the particle scattering model used by L. Boltzmann to prove his famed *H-theorem* (1872). Besides all the historic significance of that theorem, the model used by Boltzmann (see Sec. 6.2 below) is almost as cartoonish.

systems, in thermodynamic equilibrium at temperature T that is comparable with the energy gap Δ . For each variable, sketch its temperature dependence, and find its asymptotic values (or trends) in the low-temperature and high-temperature limits.

Hint: The two-level system is generally defined as any system with just two relevant states whose energies, say E_0 and E_1 , are separated by a finite gap $\Delta \equiv E_1 - E_0$. Its most popular (but not the only!) example is a spin- $1/2$ particle, e.g., an electron, in an external magnetic field.

2.3. Solve the previous problem using the Gibbs distribution. Also, calculate the probabilities of the energy level occupation, and give physical interpretations of your results, in both temperature limits.

2.4. Calculate the low-field magnetic susceptibility χ_m of a dilute set of non-interacting, spontaneous magnetic dipoles $\mathbf{m}$, in thermal equilibrium at temperature T , within two models:

- (i) the dipole moment $\mathbf{m}$ is a classical vector of fixed magnitude m_0 , but arbitrary orientation, and
- (ii) the dipole moment $\mathbf{m}$ belongs to a quantum spin- $1/2$ particle, and is described by vector operator $\hat{\mathbf{m}} = \gamma \hat{\mathbf{S}}$, where γ is the gyromagnetic ratio, and $\hat{\mathbf{S}}$ is the vector operator of particle's spin.⁷⁴

Hint: The low-field magnetic susceptibility of an isotropic medium is defined⁷⁵ as

$$\chi_m \equiv \frac{\partial M_z}{\partial \mathcal{H}},$$

where $\mathbf{M}$ is the (average) magnetization of a unit volume, and axis z is aligned with the direction of the external magnetic field $\mathcal{H}$.

2.5. Calculate the low-field magnetic susceptibility of a set of non-interacting, distinguishable particles with an arbitrary spin s , neglecting their orbital motion. Compare the result with the solution of the previous problem.

Hint: Quantum mechanics⁷⁶ tells us that the Cartesian component m_z of the magnetic moment of such a particle, in the direction of the applied field, may take $(2s + 1)$ values

$$m_z = \gamma \hbar s_m, \quad \text{where } s_m = -s, -s + 1, \dots, s - 1, s,$$

where γ is the gyromagnetic ratio of the particle, and $\hbar$ is the Planck's constant.

2.6.* Derive a general expression for the average interaction potential between two similar magnetic dipoles with fixed magnitude m but arbitrary orientation, at thermal equilibrium. Spell out the result in the low-temperature and high-temperature limits.

2.7.* Analyze the possibility of using a system of non-interacting spin- $1/2$ particles in magnetic field for refrigeration.

Hint: See a footnote in Sec. 1.6.

⁷⁴ See, e.g., QM Sec. 4.4. Note that both models assume that the particle's orbital motion (if any) does not contribute to its magnetic moment.

⁷⁵ See, e.g., EM Sec. 5.5, in particular Eq. (5.111).

⁷⁶ See, e.g., QM Sec. 5.7, in particular Eq. (5.197).

2.8. Use the microcanonical distribution to calculate the average entropy, energy, and pressure of a single classical particle of mass m , with no internal degrees of freedom, free to move in volume V , at temperature T .

Hint: Try to make a more accurate calculation than has been done in Sec. 2.2 for the system of N harmonic oscillators. For that you will need to know the volume V_d of an d -dimensional hypersphere of the unit radius. To avoid being too cruel, I am giving it to you:

$$V_d = \pi^{d/2} / \Gamma\left(\frac{d}{2} + 1\right),$$

where $\Gamma(\xi)$ is the gamma-function.⁷⁷

2.9. Solve the previous problem starting from the Gibbs distribution.

2.10. Calculate the average energy, entropy, free energy, and the equation of state of a classical 2D particle (without internal degrees of freedom), free to move within area A , at temperature T , starting from:

- (i) the microcanonical distribution, and
- (ii) the Gibbs distribution.

Hint: Make the appropriate modification of the notion of pressure.

2.11. A quantum particle of mass m is confined to free motion along a 1D segment of length a . Using any approach you like, find the average force the particle exerts on walls of such a “1D quantum well” in thermal equilibrium, and analyze its temperature dependence, focusing on the low-temperature and high-temperature limits.

Hint: You may consider series $\Theta(\xi) \equiv \sum_{n=1}^{\infty} e^{-\xi n^2}$ as a known function of ξ .⁷⁸

2.12. Rotational properties of diatomic molecules (such as N_2 , CO , etc.) may be reasonably well described using a “dumbbell” model: two point particles, of masses m_1 and m_2 , with a fixed distance d between them. Ignoring the translational motion of the molecule as the whole, use this model to calculate its heat capacity, and spell out the result in the limits of low and high temperatures. (Quantify the conditions.)

2.13. Calculate the heat capacity of a diatomic molecule, using the simple model described in the previous problem, but now assuming that the rotation is confined to one plane.⁷⁹

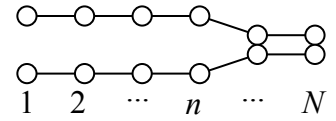
⁷⁷ For its definition and main properties, see, e.g., MA Eqs. (6.6)-(6.9).

⁷⁸ It may be reduced to the so-called elliptic theta-function $\theta_3(z, \tau)$ for a particular case $z = 0$ - see, e.g., Sec. 16.27 in the Abramowitz-Stegun handbook cited in MA Sec. 16(ii). However, you do not need that (or any other :-)

handbook to solve this problem.
⁷⁹ This is a reasonable model of the constraints imposed on small atomic groups (e.g., ligands) by their environment inside some large molecules.

2.14. Low-temperature specific heat of some solids has a considerable contribution from thermal excitation of spin waves, whose dispersion law scales as $\omega \propto k^2$ at $\omega \rightarrow 0$.⁸⁰ Find the temperature dependence of this contribution to C_V at low temperatures and discuss conditions of its experimental observation.

2.15. A rudimentary “zipper” model of DNA replication is a chain of N links that may be either open or closed - see Fig. on the right. Opening a link increases system’s energy by $\Delta > 0$, and a link may change its state (either open or close) only if all links to the left of it are already open. Calculate the average number of open links at thermal equilibrium, and analyze its temperature dependence in detail, especially for the case $N \gg 1$.



2.16. An ensemble of classical 1D particles of mass m , residing in the potential wells

$$U(x) = \alpha |x|^\gamma, \quad \text{with } \gamma > 0,$$

is in thermal equilibrium at temperature T . Calculate the average values of its potential energy U and the full energy E using two approaches:

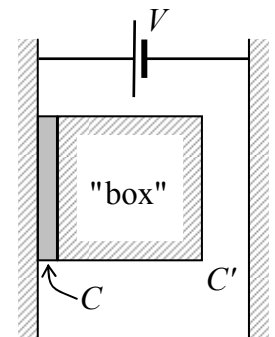
- (i) directly from the Gibbs distribution, and
- (ii) using the virial theorem of classical mechanics.⁸¹

2.17. For a thermally-equilibrium ensemble of slightly anharmonic classical 1D oscillators, with mass m and potential energy

$$U(q) = \frac{\kappa}{2} q^2 + \alpha q^3,$$

with small coefficient α , calculate $\langle x \rangle$ in the first approximation in low temperature T .

2.18.* A small conductor (in this context, usually called the *single-electron box*) is placed between two conducting electrodes, with voltage V applied between them. The gap between one of the electrodes and the island is so narrow that electrons may tunnel quantum-mechanically through this gap (“weak tunnel junction”) – see Fig. on the right. Calculate the average charge of the island as a function of V .



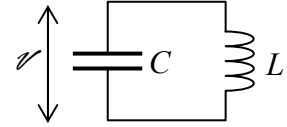
Hint: The quantum-mechanical tunneling of electrons through weak junctions⁸² between macroscopic conductors, and its subsequent energy relaxation inside the conductor, may be considered as a single inelastic (energy-dissipating) event, so that the only energy relevant for the thermal equilibrium of the system is its electrostatic potential energy.

⁸⁰ Note that by the same dispersion law is typical for elastic bending waves in thin rods – see, e.g., CM Sec. 7.8.

⁸¹ See, e.g., CM Problem 1.12.

⁸² In this context, weak junction means a tunnel junction with transparency so low that the tunneling electron’s wavefunction loses its quantum-mechanical coherence before the electron has time to tunnel back. In a typical junction of a macroscopic area this condition is fulfilled if the effective tunnel resistance of the junction is much higher than the quantum unit of resistance (see, e.g., QM Sec. 3.2), $R_Q \equiv \pi \hbar / 2e^2 \approx 6.5 \text{ k}\Omega$.

2.19. An LC circuit (see Fig. on the right) is at thermodynamic equilibrium with the environment. Find the r.m.s. fluctuation $\delta\mathcal{V} \equiv \langle \mathcal{V}^2 \rangle^{1/2}$ of the voltage across it, for an arbitrary ratio $T/\hbar\omega$, where $\omega = (LC)^{-1/2}$ is the resonance frequency of this “tank circuit”.



2.20. Derive Eq. (92) from simplistic arguments, representing the blackbody radiation as an ideal gas of photons, treated as ultrarelativistic particles. What do similar arguments give for an ideal gas of classical, nonrelativistic particles?

2.21. Calculate the enthalpy, the entropy, and the Gibbs energy of the blackbody electromagnetic radiation with temperature T , and then use these results to find the law of temperature and pressure drop at an adiabatic expansion of the radiation.

2.22. As was mentioned in Sec. 2.6(i) of the lecture notes, the relation between the visible temperatures $T_\odot$ of Sun’s surface and Earth’s surface T_0 follows from the balance of the thermal radiation they emit. Prove that this relation indeed follows, with a good precision, from a simple model in which the surfaces radiate as perfect black bodies with a constant, average temperature.

Hint: You may pick up the experimental values you need from any (reliable :-) source.

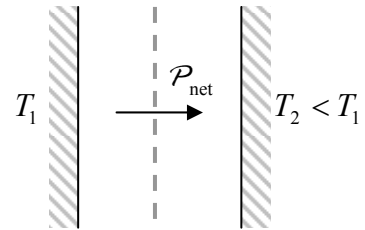
2.23. If a surface is not perfectly radiation-absorbing (“black”), the electromagnetic power of its thermal radiation differs from the Stefan law (2.89a) by a frequency-dependent factor $\varepsilon < 1$, called *emissivity*:

$$\frac{\mathcal{P}}{A} = \varepsilon \sigma T^4.$$

Prove that such surface reflects $(1 - \varepsilon)$ part of incident radiation.

2.24. If two black surfaces, facing each other, have different temperatures (see Fig. on the right), then according to the Stefan radiation law (2.89), there is a net flow of thermal radiation, from a warmer surface to the colder one:

$$\frac{\mathcal{P}_{\text{net}}}{A} = \sigma (T_1^4 - T_2^4).$$



For many applications (including low temperature experiments) this flow is detrimental. One way to reduce it is to reduce the emissivity $e(\omega)$ of both surfaces – say by covering them with shiny metallic films. An alternative way toward the same goal is to place, between the surfaces, a thin layer (usually called the *thermal shield*), with a low emissivity of both surfaces, and disconnected from any heat bath – see dashed line in Fig. above. Assuming that the emissivity is the same in both cases, find out which way is more efficient.

Hint: The definition of emissivity may be found, for example, in the previous problem.

2.25. Two parallel, well conducting plates of area A are separated by a free-space gap of a constant thickness $t \ll A^{1/2}$. Calculate the energy of the spontaneous electromagnetic field inside the gap

at thermal equilibrium with temperature T . Specify the validity limits of your result. Does the radiation push the plates apart?

2.26. Use the Debye theory to estimate the specific heat of aluminum at room temperature (say, 300 K), and express the result in the following popular units:

- (i) eV/K per atom,
- (ii) J/K per mole, and
- (iii) J/K per gram.

Compare the last number with the experimental value (from a reliable book or online source).

2.27. Use the general Eq. (123) to re-derive the Fermi-Dirac distribution (115) for a system in equilibrium.

2.28. Each of two similar particles, not interacting directly, may take two quantum states, with single-particle energies ε equal to 0 and Δ . Write down the statistical sum Z of the system, and use it to calculate its average total energy E of the system, for the cases when the particles are:

- (i) distinguishable;
- (ii) indistinguishable fermions;
- (iii) indistinguishable bosons.

Analyze and interpret the temperature dependence of $\langle E \rangle$ for each case, assuming that $\Delta > 0$.

2.29. Calculate the chemical potential of a system of $N \gg 1$ independent fermions, kept at fixed temperature T , provided that each particle has two non-degenerate energy levels, separated by gap Δ .

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Chapter 3. Ideal and Not-So-Ideal Gases

In this chapter, the general approaches discussed in the previous chapters are applied to calculate statistical and thermodynamic properties of gases, i.e. collections of identical particles (say, atoms or molecules) that are free to move inside a certain volume, either not interacting or weakly interacting with each other.

3.1. Ideal classical gas

Interactions of typical atoms and molecules are well localized, i.e. rapidly decreasing with distance r between them, becoming negligible at certain distance r_0 . In a gas of N particles inside volume V , the average distance $\langle r \rangle$ between the particles is of the order of $(V/N)^{1/3}$. As a result, if the gas density $n \equiv N/V \sim \langle r \rangle^{-3}$ is much lower than r_0^{-3} , i.e. if $nr_0^3 \ll 1$, the chance for its particles to approach each other and interact is rather small. The model in which such interactions are completely ignored is called the *ideal gas*.

Let us start with a *classical* ideal gas, which may be defined as the gas in whose behavior the quantum effects are negligible. As we saw in Sec. 2.8, the condition of that is to have the average occupancy of each quantum state low:

$$\langle N_k \rangle \ll 1. \quad (3.1)$$

It may seem that we have already found properties of such a system, in particular the equilibrium occupancy of its states – see Eq. (2.111):

$$\langle N_k \rangle = \text{const} \times \exp \left\{ -\frac{\varepsilon_k}{T} \right\}. \quad (3.2)$$

In some sense it is true, but we still need, first, to see what exactly does Eq. (2) means for the gas, i.e. a system with an essentially continuous energy spectrum, and, second, to show that, rather surprisingly, particles' indistinguishability affects some properties of even classical gases.

The first of these tasks is evidently the easiest for a gas out of external fields, and with no internal degrees of freedom.¹ In this case ε_k is just the kinetic energy of the particle obeys the isotropic and parabolic dispersion law

$$\varepsilon_k = \frac{p^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}. \quad (3.3)$$

Now we have to use two facts from other fields of physics. First, in quantum mechanics, momentum $\mathbf{p}$ is associated with wavevector $\mathbf{k}$ of the de Broglie wave, $\mathbf{p} = \hbar \mathbf{k}$.² Second, eigenvalues of $\mathbf{k}$ for *any* waves (including de Broglie waves) in free space are uniformly distributed in the momentum space, with a constant density of states, given by Eq. (2.82)

¹ In more realistic cases when particles do have internal degrees of freedom, but they are in certain (say, ground) quantum states, Eq. (3) is valid as well, with ε_k referred to the internal ground-state energy.

² See, e.g., QM Sec. 1.2.

$$\frac{dN_{\text{states}}}{d^3k} = \frac{gV}{(2\pi)^3}, \quad \text{i.e.} \quad \frac{dN_{\text{states}}}{d^3p} = \frac{gV}{(2\pi\hbar)^3}, \quad (3.4)$$

where g is the degeneracy of particle's internal states (say, for electrons, the spin degeneracy $g = 2$).

Even regardless of the exact proportionality coefficient between dN_{states} and d^3p , the very fact of this proportionality means that the probability dW to find the particle in a small region $d^3p = dp_1 dp_2 dp_3$ of the momentum space is proportional to the right-hand part of Eq. (2), with ε_k given by Eq. (3):

$$dW = C \exp\left\{-\frac{p^2}{2mT}\right\} d^3p = C \exp\left\{-\frac{p_1^2 + p_2^2 + p_3^2}{2mT}\right\} dp_1 dp_2 dp_3. \quad (3.5)$$

Maxwell
distribution

This is the famous *Maxwell distribution*.³ The normalization constant C may be readily found from the last form of Eq. (5), by requiring that the integral of dW over all the momentum space to equal 1, and using the equality of all 1D integrals over the each Cartesian component p_j of the momentum ($j = 1, 2, 3$), which may be reduced to the well-known dimensionless Gaussian integral:⁴

$$C = \left[\int_{-\infty}^{+\infty} \exp\left\{-\frac{p_j^2}{2mT}\right\} dp_j \right]^{-3} = \left[(2mT)^{1/2} \int_{-\infty}^{+\infty} e^{-\xi^2} d\xi \right]^{-3} = (2\pi mT)^{-3/2}. \quad (3.6)$$

As a sanity check, let us use the Maxwell distribution to calculate the average energy corresponding to each half-degree of freedom:

$$\left\langle \frac{p_j^2}{2m} \right\rangle = \int \frac{p_j^2}{2m} dW = \left[C^{1/3} \int_{-\infty}^{+\infty} \frac{p_j^2}{2m} \exp\left\{-\frac{p_j^2}{2mT}\right\} dp_j \right] \left[C^{1/3} \int_{-\infty}^{+\infty} \exp\left\{-\frac{p_{j'}^2}{2mT}\right\} dp_{j'} \right]^2 = \frac{T}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \xi^2 e^{-\xi^2} d\xi. \quad (3.7)$$

The last integral⁵ equals $\sqrt{\pi}/2$, so that, finally,

$$\left\langle \frac{p_j^2}{2m} \right\rangle \equiv \left\langle \frac{mv_j^2}{2} \right\rangle = \frac{T}{2}. \quad (3.8)$$

This result is (fortunately :-)) in agreement with the equipartition theorem (2.48). It also means that the r.m.s. velocity of the particles is

$$\delta v \equiv \langle v^2 \rangle^{1/2} = \left\langle \sum_{j=1}^3 v_j^2 \right\rangle^{1/2} = \langle 3v_j^2 \rangle^{1/2} = \left(3 \frac{T}{m} \right)^{1/2}. \quad (3.9)$$

³ This formula was suggested by J. C. Maxwell as early as in 1860, i.e. well before the Boltzmann and Gibbs distributions. Note also that the term “Maxwell distribution” is often associated with the distribution of particle's momentum (or velocity) *magnitude*,

$$dW = 4\pi C p^2 \exp\left\{-\frac{p^2}{2mT}\right\} dp = 4\pi C m^3 v^2 \exp\left\{-\frac{mv^2}{2T}\right\} dv, \quad \text{with } 0 \leq p, v < \infty,$$

which immediately follows from Eq. (5) combined with the expression $d^3p = 4\pi p^2 dp$ due to the spherical symmetry of the distribution in the momentum/velocity space.

⁴ See, e.g., MA Eq. (6.9b).

⁵ See, e.g., MA Eq. (6.9c).

For a typical gas (say, N_2), with $m \approx 28 m_p \approx 4.7 \times 10^{-26}$ kg at room temperature ($T = k_B T_K \approx k_B \times 300 \text{ K} \approx 4.1 \times 10^{-21}$ J), this velocity is about 500 m/s – comparable with the sound velocity in the same gas (and the muzzle velocity of typical handgun bullets). Still, it is measurable using simple table-top equipment (say, a set of two concentric, rapidly rotating cylinders with a thin slit collimating an atomic beam emitted at the axis) that was available already in the end of the 19th century. Experiments using such equipment gave convincing confirmations of Maxwell's theory.

This is all very simple (isn't it?), but actually the thermodynamic properties of a classical gas, especially its entropy, are more intricate. To show that, let us apply the Gibbs distribution to gas portions consisting of N particles each, rather than just one of them. If the particles are exactly similar, the eigenenergy spectrum $\{\varepsilon_k\}$ of each of them is also exactly the same, and each value E_m of the total energy is just the sum of particular energies $\varepsilon_{k(l)}$ of the particles, where $k(l)$, with $l = 1, 2, \dots, N$, is the number of the energy level of l^{th} particle. Moreover, since the gas is classical, $\langle n_k \rangle \ll 1$, the probability of having two or more particles in any state may be ignored. As a result, we can use Eq. (2.59) to write

$$Z = \sum_m \exp\left\{-\frac{E_m}{T}\right\} = \sum_{k(l)} \exp\left\{-\frac{1}{T} \sum_l \varepsilon_{k(l)}\right\} = \sum_{k(1)} \sum_{k(2)} \dots \sum_{k(N)} \prod_l \exp\left\{-\frac{\varepsilon_{k(l)}}{T}\right\}, \quad (3.10)$$

where the summation has to be carried over all possible states of each particle. Since the summation over each set $\{k(l)\}$ concerns only one of the operands of the product of exponents under the sum, it is tempting to complete the calculation as follows:

$$Z \rightarrow Z_{\text{dist}} = \sum_{k(1)} \exp\left\{-\frac{\varepsilon_{k(1)}}{T}\right\} \cdot \sum_{k(2)} \exp\left\{-\frac{\varepsilon_{k(2)}}{T}\right\} \dots \sum_{k(N)} \exp\left\{-\frac{\varepsilon_{k(N)}}{T}\right\} = \left(\sum_k \exp\left\{-\frac{\varepsilon_k}{T}\right\} \right)^N, \quad (3.11)$$

where the final summation is over all states of one particle. This formula is indeed valid for distinguishable particles.⁶ However, if particles are indistinguishable (again, meaning that they are identical *and* free to move within the same spatial region), Eq. (11) has to be modified by what is called the *correct Boltzmann counting*:

Correct
Boltzmann
counting

$$Z = \frac{1}{N!} \left(\sum_k \exp\left\{-\frac{\varepsilon_k}{T}\right\} \right)^N, \quad (3.12)$$

that considers all quantum states, differing only by particle permutations in the gas portion, as one.

Now let us take into account that the fundamental relation (4) implies the following rule for the replacement of a sum over quantum states with an integral in the classical limit - whose exact conditions are still to be specified:⁷

$$\sum_k (...) \rightarrow \int (...) dN_{\text{states}} = \frac{gV}{(2\pi)^3} \int (...) d^3k = \frac{gV}{(2\pi\hbar)^3} \int (...) d^3p. \quad (3.13)$$

In application to Eq. (12), this rule yields

⁶ Since each particle belongs to the same portion of gas, i.e. cannot be distinguished from others by its spatial position, this requires some internal “pencil mark”, for example a specific structure or a specific quantum state of its internal degrees of freedom.

⁷ As a reminder, we have already used this rule (twice) in Sec. 2.6, with particular values of g .

$$Z = \frac{1}{N!} \left(\frac{gV}{(2\pi\hbar)^3} \left[\int_{-\infty}^{+\infty} \exp\left\{-\frac{p_j^2}{2mT}\right\} dp_j \right]^3 \right)^N. \quad (3.14)$$

The integral in square brackets is the same one as in Eq. (6), i.e. equal to $(2\pi mT)^{1/2}$, so that finally

$$Z = \frac{1}{N!} \left(\frac{gV}{(2\pi\hbar)^3} (2\pi mT)^{3/2} \right)^N = \frac{1}{N!} \left[gV \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} \right]^N. \quad (3.15)$$

Now, assuming that $N \gg 1$,⁸ and applying the Stirling formula, we can calculate gas' free energy,

$$F = T \ln \frac{1}{Z} = -NT \ln \frac{V}{N} + Nf(T), \quad (3.16a)$$

with

$$f(T) \equiv -T \left\{ \ln \left[g \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} \right] + 1 \right\}. \quad (3.16b)$$

The first of these relations is exactly Eq. (1.45) which was derived, in Sec. 1.4, from the equation of state $PV = NT$, using thermodynamic identities. At that stage this equation of state was just postulated, but now we can finally *derive* it by calculating pressure from the second of Eqs. (1.35), and Eq. (16a):

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{NT}{V}. \quad (3.17)$$

So, the equation of state of the ideal classical gas, with density $n \equiv N/V$, is indeed given by Eq. (1.44):

$$P = \frac{NT}{V} \equiv nT. \quad (3.18)$$

Hence we may use Eqs. (1.46)-(1.51), derived from this equation of state, to calculate all other thermodynamic variables of the gas. As one more sanity check, let us start with energy. Using Eq. (1.47) with $f(T)$ given by Eq. (16b), we immediately get

$$E = N \left(f - T \frac{df}{dT} \right) = \frac{3}{2} NT, \quad (3.19)$$

in full agreement with Eq. (8) and hence with the equipartition theorem. Much less trivial is the result for entropy, which may be obtained by combining Eqs. (1.46) and (15):

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = N \left[\ln \frac{V}{N} - \frac{df(T)}{dT} \right]. \quad (3.20)$$

⁸ For the opposite limit when $N = g = 1$, Eq. (15) yields the results obtained, by two alternative methods, in Problems 2.5 and 2.6. For $N = 1$, the “correct Boltzmann counting” factor $N!$ equals 1, so that the particle distinguishability effects vanish - naturally.

This formula,⁹ in particular, provides the means to resolve the following *gas mixing paradox* (sometimes called the “Gibbs paradox”). Consider two volumes, V_1 and V_2 , separated by a partition, each filled with the same gas, with the same density n , at the same temperature T . Now let us remove the partition and let the gases mix; would the total entropy change? According to Eq. (20), it would not, because the ratio $V/N = n$, and hence the expression in square brackets is the same in the initial and the final state, so that the entropy is additive (extensive). This makes full sense if the gas particles in the both parts of the volume are identical, i.e. the partition’s removal does not change our information about the system. However, let us assume that all particles are distinguishable; then the entropy should clearly increase, because the mixing would certainly decrease our information about the system, i.e. increase its disorder. A quantitative description of this effect may be obtained using Eq. (11). Repeating for Z_{dist} all the calculations made above for Z , we readily get a different formula for entropy:

$$S_{\text{dist}} = N \left[\ln V - \frac{df_{\text{dist}}(T)}{dT} \right], \quad f_{\text{dist}}(T) \equiv -T \ln \left[g \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} \right]. \quad (3.21)$$

Notice that in contrast to the S given by Eq. (20), entropy S_{dist} is *not* proportional to N (at fixed temperature T and density N/V). While for distinguishable particles this fact does not present any conceptual problem, for indistinguishable particles it would mean that entropy were not an extensive variable, i.e. would contradict the basic assumptions of thermodynamics. This fact emphasizes again the necessity of the correct Boltzmann counting in the latter case.

Comparing Eqs. (20) and (21), we can calculate the change of entropy due to mixing of distinguishable particles:

$$\Delta S_{\text{dist}} = (N_1 + N_2) \ln(V_1 + V_2) - (N_1 \ln V_1 + N_2 \ln V_2) = N_1 \ln \frac{V_1 + V_2}{V_1} + N_2 \ln \frac{V_1 + V_2}{V_2} > 0. \quad (3.22)$$

Note that for a particular case, $V_1 = V_2 = V/2$, Eq. (22) reduces to the simple result $\Delta S_{\text{dist}} = (N_1 + N_2) \ln 2$, which may be readily understood from the point of view of information theory. Indeed, allowing each particle of $N = N_1 + N_2$ to spread to twice larger volume, we loose one bit of information per particle, i.e. $\Delta I = (N_1 + N_2)$ bits for the whole system.

Let me leave it for the reader to show that result (22) is also valid if particles in each sub-volume are indistinguishable from each other, but different from those in another sub-volume, i.e. for mixing of two different gases.¹⁰ However, it is certainly *not* applicable to the system where *all* particles are identical, stressing again that the correct Boltzmann counting (12) does indeed affect entropy, even though it is not essential for either the Maxwell distribution (5), or the equation of state (18), or average energy (19).

In this context, one may wonder whether the change (22) (called the *mixing entropy*) is experimentally observable. The answer is yes. For example, after free mixing of two different gases one can use a thin movable membrane that is *semipermeable*, i.e. penetrable by particles of one type only, to

⁹ The result presented by Eq. (20), with function f given by Eq. (16b), was obtained independently by O. Sackur and H. Tetrode in 1911, i.e. well before the final formulation of quantum mechanics in the late 1920s.

¹⁰ By the way, if an ideal classical gas consists of particles of several different sorts, its full pressure is a sum of independent *partial pressures* exerted by each component – the so-called *Dalton law*. While this fact was an important experimental discovery in the early 1800s, from the point of view of statistical physics this is just a straightforward corollary of Eq. (18), because in an ideal gas, the component particles do not interact.

separate them again, thus reducing the entropy back to the initial value, and measure either the necessary mechanical work $\Delta \mathcal{W} = T\Delta S_{\text{dist}}$ or the corresponding heat discharge into the heat bath. Practically, measurements of this type are easier in *weak solutions*,¹¹ systems with a small concentration $c \ll 1$ of particles of one sort (*solute*) within much more abundant particles of another sort (*solvent*). The mixing entropy also affects thermodynamics of chemical reactions in gases and liquids.¹² It is curious that besides purely thermal measurements, mixing entropy in some conducting solutions (*electrolytes*) is also measurable by a purely electrical method, called *cyclic voltammetry*, in which a low-frequency ac voltage, applied between solid-state electrodes embedded in the solution, is used to periodically separate different ions, and then mix them again.¹³

Now let us briefly discuss two generalizations of our results for ideal classical gases. First, let us consider the ideal classical gas in an external field of potential forces. It may be described by replacing Eq. (3) with

$$\varepsilon_k = \frac{p_k^2}{2m} + U(\mathbf{r}_k), \quad (3.23)$$

where $\mathbf{r}_k$ is the position of the particular particle, and $U(\mathbf{r})$ is the potential energy per particle. In this cases, Eq. (4) is applicable only to small volumes, $V \rightarrow dV = d^3r$ whose linear size is much smaller than the spatial scale of variations of macroscopic parameters of the gas- say, pressure. Hence, instead of Eq. (5), we may only write the probability dW of finding the particle in a small volume d^3rd^3p of the 6-dimensional phase space:

$$dW = w(\mathbf{r}, \mathbf{p}) d^3r d^3p, \quad w(\mathbf{r}, \mathbf{p}) = \text{const} \times \exp \left\{ -\frac{p^2}{2mT} - \frac{U(\mathbf{r})}{T} \right\}. \quad (3.24)$$

Hence, the Maxwell distribution of particle velocities is still valid at each point $\mathbf{r}$, and a more interesting issue here is the spatial distribution of the total density,

$$n(\mathbf{r}) \equiv N \int w(\mathbf{r}, \mathbf{p}) d^3p, \quad (3.25)$$

of all gas particles, regardless of their momentum. For this variable, Eq. (24) yields¹⁴

$$n(\mathbf{r}) = n(0) \exp \left\{ -\frac{U(\mathbf{r})}{T} \right\}, \quad (3.26)$$

¹¹ It is interesting that statistical mechanics of weak solutions is very similar to that of ideal gases, with Eq. (18) recast into the following formula (derived in 1885 by J. van't Hoff), $PV = cNT$, for the partial pressure of the solute. One of its corollaries is that the net force (called the *osmotic pressure*) exerted on a semipermeable membrane is proportional to the difference of solute concentrations it is supporting.

¹² Unfortunately, I do not have time for even a brief introduction into this important field, and have to refer the interested reader to specialized textbooks – for example, P. A. Rock, *Chemical Thermodynamics*, University Science Books, 1983; or P. Atkins, *Physical Chemistry*, 5th ed., Freeman, 1994; or G. M. Barrow, *Physical Chemistry*, 6th ed., McGraw-Hill, 1996.

¹³ See, e.g., either Chapter 6 in A. Bard and L. Falkner, *Electrochemical Methods*, 2nd ed., Wiley, 2000 (which is a good introduction to electrochemistry as the whole); or Sec. II.8.3.1 in F. Scholz (ed.), *Electroanalytical Methods*, 2nd ed., Springer, 2010.

¹⁴ In some textbooks, Eq. (26) is also called the *Boltzmann distribution*, though it certainly should be distinguished from the more general Eq. (2.111).

where the potential energy reference is at the origin. As we will see in Chapter 6, in a non-uniform gas the equation of state (18) is valid locally if particles' *mean free path* l is much smaller than the spatial scale of changes of function $n(\mathbf{r})$.¹⁵ In this case, the local gas pressure may be still calculated from Eq. (18):

$$P(\mathbf{r}) = n(\mathbf{r})T = P(0) \exp\left\{-\frac{U(\mathbf{r})}{T}\right\}. \quad (3.27)$$

An important example of application of Eq. (27) is an approximate description of the Earth atmosphere. At all heights $h \ll R_E \sim 6 \times 10^6$ m above the Earth's surface (say, the sea level), we may describe the Earth gravity effect by potential $U = mgh$, and Eq. (27) yields the so-called *barometric formula*

$$P(h) = P(0) \exp\left\{-\frac{h}{h_0}\right\}, \quad \text{with } h_0 \equiv \frac{T}{mg} = \frac{k_B T_K}{mg}. \quad (3.28)$$

For the same N_2 (the main component of the atmosphere) at $T_K = 300$ K, $h_0 \approx 7$ km. This gives the right order of magnitude of the Earth atmosphere's thickness, though the exact law of pressure change differs somewhat from Eq. (28) because of a certain drop of the absolute temperature T with height, by about 20% at $h \sim h_0$.¹⁶

The second generalization I would like to mention is to particles with internal degrees of freedom. Ignoring, for simplicity, the potential energy $U(\mathbf{r})$, we may describe them by replacing Eq. (3) for

$$\varepsilon_k = \frac{p^2}{2m} + \varepsilon_k', \quad (3.29)$$

where ε_k' describes the internal energy of the k -th particle. If the particles are similar, we may repeat all above calculations, and see that all the results (including the Maxwell distribution) are still valid, with the only exception of Eq. (16) that now becomes

$$f(T) = -T \left\{ \ln \left[g \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} \times \sum_{\varepsilon_k'} \exp\left\{-\frac{\varepsilon_k'}{T}\right\} \right] + 1 \right\}, \quad (3.30)$$

As we already know from Eq. (1.51), this change may affect both heat capacities of the gas, C_V and C_P , but not their difference (equal to N).

3.2. Calculating μ

Now let us return to Eq. (3), i.e. neglect the external field effects, as well as thermal activation of the internal degrees of freedom, and discuss properties of ideal gases of indistinguishable quantum

¹⁵ The mean free path may be defined by the geometric relation $n\sigma l = 1$, where σ is the full cross-section of the particle-particle scattering - see, e.g., CM 3.7.

¹⁶ The reason of the drop is that the atmosphere, including molecules such as H_2O , CO_2 , etc., absorbs Sun's radiation at wavelengths ~ 500 nm much smaller than those of the back-radiation of the Earth surface, with the spectrum centered at wavelength ~ 10 μm - see Eq. (2.87) and its discussion.

particles in more detail, paying special attention to the chemical potential μ - which, as you may recall, was a little bit mysterious aspect of the Fermi and Bose distributions.

Let us start from the classical gas, and recall the conclusion of thermodynamics that μ is the Gibbs potential per unit particle – see Eq. (1.56). Hence we can calculate $\mu = G/N$ from Eqs. (1.49) and (16b). The result,

$$\mu = -T \ln \frac{V}{N} + f(T) + T = T \ln \left[\frac{N}{gV} \left(\frac{2\pi\hbar^2}{mT} \right)^{3/2} \right], \quad (3.31)$$

which may be rewritten as

$$\exp\left\{\frac{\mu}{T}\right\} = \frac{N}{gV} \left(\frac{2\pi\hbar^2}{mT} \right)^{3/2}, \quad (3.32)$$

is very important, because it gives us some information about μ not only for a classical gas, but for quantum (Fermi and Bose) gases as well. Indeed, we already know that for indistinguishable particles the Boltzmann distribution (2.111) is valid only if $\langle N_k \rangle \ll 1$. Comparing this condition with quantum statistics (2.115) and (2.118), we see that the condition of gas' classicity may be expressed as

$$\exp\left\{\frac{\mu - \varepsilon_k}{T}\right\} \ll 1 \quad (3.33)$$

for all ε_k . Since the lowest value of ε_k given by Eq. (3) is zero, Eq. (35) for a gas may be satisfied only if $\exp\{\mu/T\} \ll 1$. This means that the chemical potential of the classical has to be not just negative, but also “strongly negative” in the sense

$$-\mu \gg T. \quad (3.34)$$

According to Eq. (32), this condition may be presented as

$$T \gg T_0, \quad (3.35)$$

with T_0 defined as

$$T_0 \equiv \frac{\hbar^2}{m} \left(\frac{n}{g} \right)^{2/3} = \frac{\hbar^2}{g^{2/3} m r_A^2}, \quad \text{with } r_A \equiv \frac{1}{n^{1/3}} = \left(\frac{V}{N} \right)^{1/3}. \quad (3.36)$$

Quantum
scale of
temperature

Condition (35) is very transparent physically: disregarding factor $g^{2/3}$ (which is typically not much larger than 1), it means that the average thermal energy of a particle (which is of the order of T) has to be much larger than the energy of quantization of particle's motion at length r_A - the average distance between the particles. An alternative form of this condition is¹⁷

$$r_A \gg g^{-1/3} r_c, \quad \text{with } r_c \equiv \frac{\hbar}{(mT)^{1/2}}. \quad (3.37)$$

¹⁷ In quantum mechanics, parameter r_c so defined is frequently called the *correlation length* – see, e.g., QM Sec. 7.2 and in particular Eq. (7.37).

For a typical gas (say, N_2 , with $m \approx 14 m_p \approx 2.3 \times 10^{-26}$ kg) at the standard room temperature ($T = k_B \times 300K \approx 4.1 \times 10^{-21}$ J), $r_c \approx 10^{-11}$ m, i.e. is significantly smaller than the physical size $a \sim 3 \times 10^{-10}$ m of the molecule. This estimate shows that at room temperature, as soon as any practical gas is rare enough to be ideal ($r_A \gg a$), it is classical, i.e. the only way to observe the quantum effects in the translation motion of molecules is a very deep refrigeration. According to Eq. (36), for the same nitrogen molecule, taking $r_A \sim 10^3 a \sim 10^{-7}$ m (to ensure that direct interaction effects are negligible), T_0 should be well below 1 μ K.

In order to analyze quantitatively what happens with gases when T is reduced to such low values, we need to calculate μ for an arbitrary ideal gas of indistinguishable particles. Let us use the lucky fact that the Fermi-Dirac and the Bose-Einstein statistics may be represented with one formula:

$$\langle N(\varepsilon) \rangle = \frac{1}{e^{(\varepsilon - \mu)/T} \pm 1}, \quad (3.38)$$

where (and everywhere in the balance of this section) the top sign stands for fermions and the lower one is for bosons, to discuss the fermionic and bosonic gases on the same breath.

If we deal with a member of the grand canonical ensemble (Fig. 13), in which μ is externally fixed, we may apply Eq. (39) to calculate the *average* number N of particles in volume V . If the volume is so large that $N \gg 1$, we may use the general state counting rule (13):

$$N = \frac{gV}{(2\pi)^3} \int \langle N(\varepsilon) \rangle d^3k = \frac{gV}{(2\pi\hbar)^3} \int \frac{d^3p}{e^{[\varepsilon(p) - \mu]/T} \pm 1} = \frac{gV}{(2\pi\hbar)^3} \int_0^\infty \frac{4\pi p^2 dp}{e^{[\varepsilon(p) - \mu]/T} \pm 1}. \quad (3.39)$$

In most practical cases, however, the number N of gas particles is fixed by particle confinement (i.e. the gas portion under study is a member of the canonical ensemble – see Fig. 2.6), and hence μ rather than N should be calculated. Here comes the main trick: if N is very large, the relative fluctuation of the particle number is negligibly small ($\sim 1/\sqrt{N} \ll 1$), and the relation between the *average* values of N and μ should not depend which of these variables is exactly fixed. Hence, Eq. (39), with μ having the sense of the *average* chemical potential, should be valid even if N is exactly fixed, so that small fluctuations of N are replaced with (equally small) fluctuations of μ . Physically (as was already mentioned in Sec. 2.8), in this case the role of the μ -fixing environment for any gas sub-portion is played by the rest of the gas, and Eq. (39) expresses the condition of self-consistency of such mutual particle exchange.

In this situation, Eq. (39) may be used for calculating the average μ as a function of two independent parameters: N (i.e. of the gas density $n = N/V$) and temperature T . For carrying out this calculation, it is convenient to convert the right-hand part of Eq. (39) to an integral over particle's energy $\varepsilon(p) = p^2/2m$, so that $p = (2m\varepsilon)^{1/2}$, and $dp = (m/2\varepsilon)^{1/2} d\varepsilon$.

$$N = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{(\varepsilon - \mu)/T} \pm 1}. \quad (3.40)$$

This key result may be presented in two more convenient forms. First, Eq. (40), derived for our current (3D, isotropic and parabolic-dispersion) approximation (3), is just particular case of a general relation

$$N = \int_0^\infty g(\varepsilon) \langle N(\varepsilon) \rangle d\varepsilon, \quad (3.41)$$

Basic
equation
for μ

where

$$g(\varepsilon) \equiv \frac{dN_{\text{states}}}{d\varepsilon} \quad (3.42)$$

is the temperature-independent density of all quantum states of a particle – regardless of whether they are occupied or not. Indeed, according to the general Eq. (4), for our simple model (3),

$$g(\varepsilon) = g_3(\varepsilon) \equiv \frac{dN_{\text{states}}}{d\varepsilon} = \frac{d}{d\varepsilon} \left(\frac{gV}{(2\pi\hbar)^3} \frac{4\pi}{3} p^3 \right) = \frac{4\pi gV}{3(2\pi\hbar)^3} \frac{d(p^3)}{d\varepsilon} = \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \varepsilon^{1/2}, \quad (3.43)$$

so that we return to Eq. (39). On the other hand, for some calculations, it is convenient to introduce a dimensionless energy variable $\xi \equiv \varepsilon/T$ to express Eq. (40) via a dimensionless integral:

$$N = \frac{gV(mT)^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \frac{\xi^{1/2} d\xi}{e^{\xi-\mu/T} \pm 1}. \quad (3.44)$$

As a sanity check, in the classical limit (34), the exponent in the denominator of the fraction under the integral is much larger than 1, and Eq. (44) reduces to

$$N = \frac{gV(mT)^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \frac{\xi^{1/2} d\xi}{e^{\xi-\mu/T}} \approx \frac{gV(mT)^{3/2}}{\sqrt{2}\pi^2\hbar^3} \exp\left\{\frac{\mu}{T}\right\} \int_0^\infty \xi^{1/2} e^{-\xi} d\xi, \quad \text{at } -\mu \gg T. \quad (3.45)$$

By the definition of gamma-function $\Gamma(\xi)$,¹⁸ this dimensionless integral is just $\Gamma(3/2) = \sqrt{\pi}/2$, and we get

$$\exp\left\{\frac{\mu}{T}\right\} = N \frac{\sqrt{2}\pi^2\hbar^3}{gV(mT)^{3/2}} \frac{2}{\sqrt{\pi}} = \left(2\pi \frac{T_0}{T}\right)^{3/2}, \quad (3.46)$$

which is exactly the same result as given by Eq. (34), which has been obtained in a rather different way – from the Boltzmann distribution and thermodynamic identities.

Unfortunately, in the general case of arbitrary μ the integral in Eq. (44) cannot be worked out analytically.¹⁹ The best we can do is to use temperature T_0 , defined by Eq. (37), to rewrite Eq. (44) as

$$\frac{T}{T_0} = \left[\frac{1}{\sqrt{2}\pi^2} \int_0^\infty \frac{\xi^{1/2} d\xi}{e^{\xi-\mu/T} \pm 1} \right]^{-2/3}. \quad (3.47)$$

We may use this relation to calculate ratio T/T_0 , and then ratio $\mu/T_0 \equiv (\mu/T) \times (T/T_0)$, as functions of μ/T numerically, and then plot the results versus each other, thinking of the former ratio as the argument.

Figure 1 shows the resulting plot. It shows that at large temperatures, $T \gg T_0$, the chemical potential is negative and approaches the classical behavior given by Eq. (46) for both fermions and bosons – just as we could expect. For fermions, the reduction of temperature leads to μ changing its sign from negative to positive, and then approaching a constant positive value called the *Fermi energy*, $\varepsilon_F \approx 7.595 T_0$ at $T \rightarrow 0$. On the contrary, the chemical potential of a gas of bosons stays negative, and turns

¹⁸ See, e.g., MA Eq. (6.7a).

¹⁹ For reader's reference only: for the upper sign, the integral in Eq. (40) is a particular form (for $s = 1/2$) of a special function called the *complete Fermi-Dirac integral* F_s , while for the lower sign, it is a particular case (for $s = 3/2$) of another special function called the *polylogarithm* Li_s . (In what follows, I will not use these notations.)

into zero at certain *critical temperature* $T_c \approx 3.313 T_0$. Both these limits, which are very important for applications, may (and will be :-) explored analytically, but separately for each statistics.

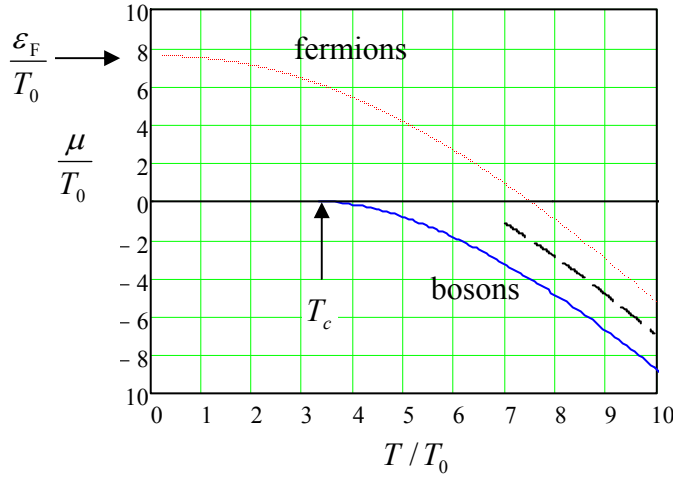


Fig. 3.1. Chemical potential of an ideal gas of $N \gg 1$ indistinguishable quantum particles, as a function of temperature (at fixed gas density $n \equiv N/V$, which fixes parameter $T_0 \propto n^{3/2}$), for two different quantum statistics. The dashed line shows the classical approximation (46) valid at $T \gg T_0$.

Before doing that (in the next two sections), let me show that, rather surprisingly, for any (but nonrelativistic!) quantum gas, the product PV expressed in terms of energy,

$$PV = \frac{2}{3} E, \quad (3.48)$$

is the same as follows from Eqs. (18) and (19) for the classical gas, and hence does *not* depend on particle's statistics. In order to prove this, it is sufficient to use Eqs. (2.114) and (2.117) for the grand thermodynamic potential of each quantum state, which may be conveniently represented by a single formula,

$$\Omega_k = \mp T \ln \left(1 \pm e^{(\mu - \varepsilon_k)/T} \right), \quad (3.49)$$

and sum them over all states k , using the general summation formula (13). The result for the total grand potential of a 3D gas with the dispersion law (3) is

$$\Omega = \mp T \frac{gV}{(2\pi\hbar)^3} \int_0^\infty \ln \left(1 \pm e^{(\mu - \varepsilon)/T} \right) 4\pi p^2 dp = \mp T \frac{gVm^{3/2}}{\sqrt{2\pi^2\hbar^3}} \int_0^\infty \ln \left(1 \pm e^{(\mu - \varepsilon)/T} \right) \varepsilon^{1/2} d\varepsilon. \quad (3.50)$$

Working out this integral by parts, exactly as we did it with the one in Eq. (2.90), we get

$$\Omega = -\frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2\pi^2\hbar^3}} \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{(\varepsilon - \mu)/T} \pm 1} = -\frac{2}{3} \int_0^\infty \varepsilon g_3(\varepsilon) \langle N(\varepsilon) \rangle d\varepsilon. \quad (3.51)$$

But the last integral is just the total energy E of the gas:

$$E = \frac{gV}{(2\pi\hbar)^3} \int_0^\infty \frac{p^2}{2m} \frac{4\pi p^2 dp}{e^{[\varepsilon(p) - \mu]/T} \pm 1} = \frac{gVm^{3/2}}{\sqrt{2\pi^2\hbar^3}} \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{(\varepsilon - \mu)/T} \pm 1} = \int_0^\infty \varepsilon g_3(\varepsilon) \langle N(\varepsilon) \rangle d\varepsilon, \quad (3.52)$$

so that for any temperature and any particle type, $\Omega = -(2/3)E$. But since, from thermodynamics, $\Omega = -PV$, we have Eq. (48) proved. This universal relation will be repeatedly used below.

PV vs. E

Ideal gas' energy

3.3. Degenerate Fermi gas

The analysis of low-temperature properties of a Fermi gas is very simple in the limit $T = 0$. Indeed, in this limit, the Fermi-Dirac distribution (2.115) is just a step function:

$$\langle N(\varepsilon) \rangle = \begin{cases} 1, & \text{for } \varepsilon < \mu, \\ 0, & \text{for } \mu < \varepsilon, \end{cases} \quad (3.53)$$

- see by the bold line in Fig. 2a. Since $\varepsilon = p^2/2m$ is isotropic in the momentum space, this means that at $T = 0$, in that space the particles fully occupy all possible quantum states within a sphere (frequently called either the *Fermi sphere* or the *Fermi sea*) with some radius p_F (Fig. 2b), while all states above the sea surface are empty. Such *degenerate Fermi gas* is a striking manifestation of the Pauli principle: though at thermodynamic equilibrium at $T = 0$ all particles try to lower their energies as much as possible, only g of them may occupy each quantum state within the Fermi sphere. As a result, the sphere's volume is proportional to the particle number N , or rather to their density $n = N/V$.

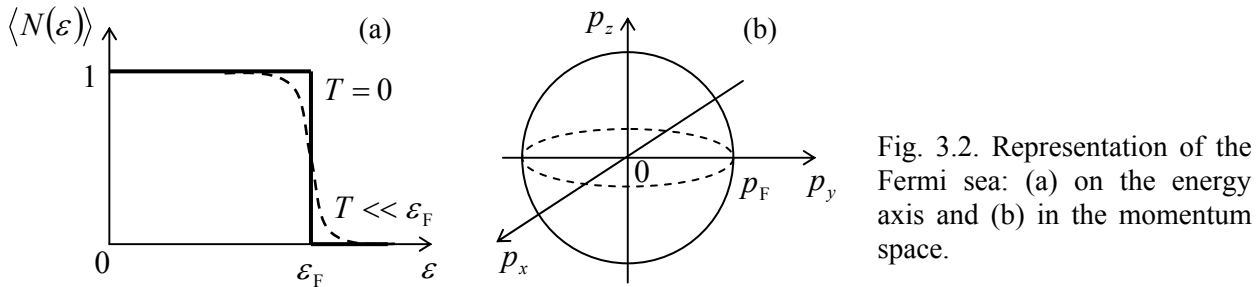


Fig. 3.2. Representation of the Fermi sea: (a) on the energy axis and (b) in the momentum space.

Indeed, radius p_F may be readily related to the number of particles N using Eq. (40) whose integral in this case is just the Fermi sphere volume:

$$N = \frac{gV}{(2\pi\hbar)^3} \int_0^{p_F} 4\pi p^2 dp = \frac{gV}{(2\pi\hbar)^3} \frac{4\pi}{3} p_F^3. \quad (3.54)$$

Now we can use Eq. (3) to express via N the chemical potential μ (which in this limit, $T \rightarrow 0$, bears the special name of the *Fermi energy* ε_F)²⁰:

$$\varepsilon_F \equiv \mu|_{T=0} = \frac{p_F^2}{2m} = \frac{\hbar^2}{2m} \left(6\pi^2 \frac{N}{gV} \right)^{2/3} = \left(\frac{9\pi^4}{2} \right)^{1/3} T_0 \approx 7.595 T_0, \quad (3.55a) \quad \text{Fermi energy}$$

where T_0 is the quantum temperature scale defined by Eq. (36). This formula quantifies the low-temperature trend of function $\mu(T)$, clearly visible in Fig. 1, and in particular explains the ratio ε_F/T mentioned in Sec. 2. Note also a useful and simple relation,

$$\varepsilon_F = \frac{3}{2} \frac{N}{g_3(\varepsilon_F)}, \quad (3.55b)$$

which may be obtained immediately from Eqs. (43) and (54).

²⁰ Note that in the electronic engineering literature, μ is usually called the *Fermi level*, at any temperature.

The total energy of the gas may be (equally easily) calculated from Eq. (52):

$$E = \frac{gV}{(2\pi\hbar)^3} \int_0^{p_F} \frac{p^2}{2m} 4\pi p^2 dp = \frac{gV}{(2\pi\hbar)^3} \frac{4\pi}{2m} \frac{p_F^5}{5} = \frac{3}{5} \varepsilon_F N, \quad (3.56)$$

showing that the average energy, $\langle \varepsilon \rangle \equiv E/N$, of a particle inside the Fermi sea is equal to $3/5 = 60\%$ of that (ε_F) of the most energetic occupied states, on the Fermi surface. Since, according to the formulas of Chapter 1, at zero temperature $H = G = N\mu$, and $F = E$, the only thermodynamic variable still to be calculated is pressure P . For that, we could use any of thermodynamic relations $P = (H - E)/V$ or $P = -(\partial F/\partial V)_T$, but it is even easier to use our recent result (48). Together with Eq. (56), it yields

$$P = \frac{2}{3} \frac{E}{V} = \frac{2}{5} \varepsilon_F \frac{N}{V} = \left(\frac{36\pi^4}{125} \right)^{1/3} P_0 \approx 3.035 P_0, \quad \text{where } P_0 \equiv nT_0 = \frac{\hbar^2}{mg^{2/3}} n^{5/3}. \quad (3.57)$$

From here, it is easy to calculate the *bulk modulus* (reciprocal *compressibility*),²¹

$$K \equiv -V \left(\frac{\partial P}{\partial V} \right)_T = \frac{2}{3} \varepsilon_F \frac{N}{V}, \quad (3.58)$$

which is simpler to measure experimentally.

Perhaps the most important example²² of the degenerate Fermi gas are the *conduction electrons* in metals – the electrons that belong to outer shells of the isolated atoms but become common in solid metals and can move through the crystal lattice almost freely. Though electrons (which are fermions with spin $s = 1/2$ and hence the spin degeneracy $g = 2s + 1 = 2$) are negatively charged, the Coulomb interaction of conduction electrons with each other is substantially compensated by the positively charged ions of the atomic lattice, so that they follow the simple formulas derived above reasonably well. This is especially true for alkali metals (forming Group 1 of the periodic table of elements), whose experimentally measured Fermi surfaces are spherical within 1% even within 0.1% for Na. Table 1 lists, in particular, the experimental values of the bulk modulus for such metals, together with the values given by Eq. (58) using ε_F calculated from Eq. (55) with the experimental density of conduction electrons. Evidently, the agreement is pretty good, taking into account that the simple theory described above completely ignores such factors as the Coulomb and exchange interactions of the electrons. This agreement implies that, surprisingly, the rigidity of solids (or at least metals) is predominantly due to the kinetic energy of conduction electrons, complemented with the Pauli principle, rather than any electrostatic interactions – though, to be fair, these interactions are the crucial factor defining the equilibrium value of n . Numerical calculations using more accurate approximations (e.g., the density functional theory²³) that agree with experiment with a few percent accuracy, confirm this conclusion.²⁴

²¹ See, e.g., CM Eq. (7.39).

²² Recently, degenerate gases (with $\varepsilon_F \sim 5T$) have been formed of weakly interacting Fermi atoms as well – see, e.g., K. Aikawa *et al.*, *Phys. Rev. Lett.* **112**, 010404 (2014) and references therein.

²³ See, e.g., QM Sec. 8.4.

²⁴ Note also a huge difference between the very high bulk modulus of metals ($K \sim 10^{11}$ Pa) and its very low values in usual gases (for them, at ambient conditions, $K \sim 10^5$ Pa). About 4 orders of magnitude of this difference is due to that in particles, density N/V , but the balance is due to the electron gas' degeneracy. Indeed, in an ideal classical gas, $K = P = NT/V$, so that factor $(2/3)\varepsilon_F$ in Eq. (58), of the order of a few eV in metals, should be compared with factor $T \sim 25$ meV in the atomic gases at room temperature.

Table 3.1. Experimental and theoretical parameters of electron's Fermi sea in some alkali metals²⁵

Metal	ε_F (eV) Eq. (55)	K (GPa) Eq. (58)	K (GPa) experiment	γ (mcal/mole·K ²) Eq. (69)	γ (mcal/mole·K ²) experiment
Na	3.24	923	642	0.26	0.35
K	2.12	319	281	0.40	0.47
Rb	1.85	230	192	0.46	0.58
Cs	1.59	154	143	0.53	0.77

Now looking at the values of ε_F listed in the table, note that room temperatures ($T_K \sim 300$ K) correspond to $T \sim 25$ meV. As a result, virtually all experiments with metals, at least in their solid or liquid form, are performed in the limit $T \ll \varepsilon_F$. According to Eq. (39), at such temperatures the occupancy step described by the Fermi-Dirac distribution has a finite but relatively small width $\sim T$ – see the dashed line in Fig. 2a. Calculations in this case are much facilitated by the so-called *Sommerfeld expansion formula*²⁶ for integrals like (40) and (52):

$$I(T) \equiv \int_0^\infty \varphi(\varepsilon) \langle N(\varepsilon) \rangle d\varepsilon \approx \int_0^\mu \varphi(\varepsilon) d\varepsilon + \frac{\pi^2}{6} T^2 \frac{d\varphi(\mu)}{d\mu}, \quad \text{at } T \ll \mu, \quad (3.59) \quad \text{Sommerfeld expansion}$$

where $\varphi(\varepsilon)$ is an arbitrary function that is sufficiently smooth at $\varepsilon = \mu$ and integrable at $\varepsilon = 0$. In order to prove this formula, let us introduce another function

$$f(\varepsilon) \equiv \int_0^\varepsilon \varphi(\varepsilon') d\varepsilon', \quad \text{so that } \varphi(\varepsilon) = \frac{df(\varepsilon)}{d\varepsilon}, \quad (3.60)$$

and work out the integral $I(T)$ by parts:

$$I(T) = \int_0^\infty \frac{df(\varepsilon)}{d\varepsilon} \langle N(\varepsilon) \rangle d\varepsilon = \int_{\varepsilon=0}^{\varepsilon=\infty} \langle N(\varepsilon) \rangle df = \left[\langle N(\varepsilon) \rangle f \right]_{\varepsilon=0}^{\varepsilon=\infty} - \int_{\varepsilon=0}^{\varepsilon=\infty} f(\varepsilon) d\langle N(\varepsilon) \rangle = \int_0^\infty f(\varepsilon) \left(-\frac{\partial \langle N(\varepsilon) \rangle}{\partial \varepsilon} \right) d\varepsilon. \quad (3.61)$$

As evident from Eq. (39) and/or Fig. 2a, at $T \ll \mu$, function $(-\partial \langle N(\varepsilon) \rangle / \partial \varepsilon)$ approaches zero for all energies, besides a narrow peak, of unit area, at $\varepsilon \approx \mu$. Hence, if we expand function $f(\varepsilon)$ in the Taylor series near this point, just a few leading terms of the expansion should give us a good approximation:

$$\begin{aligned} I(T) &\approx \int_0^\infty \left[f(\mu) + \frac{df}{d\varepsilon} \Big|_{\varepsilon=\mu} (\varepsilon - \mu) + \frac{1}{2} \frac{d^2 f}{d\varepsilon^2} \Big|_{\varepsilon=\mu} (\varepsilon - \mu)^2 \right] \left(-\frac{\partial \langle N(\varepsilon) \rangle}{\partial \varepsilon} \right) d\varepsilon \\ &= \int_0^\mu \varphi(\varepsilon') d\varepsilon' \int_0^\infty \left(-\frac{\partial \langle N(\varepsilon) \rangle}{\partial \varepsilon} \right) d\varepsilon + \varphi(\mu) \int_0^\infty (\varepsilon - \mu) \left(-\frac{\partial \langle N(\varepsilon) \rangle}{\partial \varepsilon} \right) d\varepsilon + \frac{1}{2} \frac{d\varphi(\mu)}{d\mu} \int_0^\infty (\varepsilon - \mu)^2 \left(-\frac{\partial \langle N(\varepsilon) \rangle}{\partial \varepsilon} \right) d\varepsilon. \end{aligned} \quad (3.62)$$

²⁵ Data from N. Ashcroft and N. Mermin, *Solid State Physics*, W. B. Saunders, 1976.

²⁶ Named after A. Sommerfeld, who was the first (in 1927) to apply the then-emerging quantum mechanics to degenerate Fermi gases, in particular to electron in metals, and may be credited for most of the results discussed in this section.

In the last form of this relation, the first integral over ε equals $\langle n(\varepsilon=0) \rangle - \langle n(\varepsilon=\infty) \rangle = 1$, the second one vanishes (because the function under it is asymmetric about point $\varepsilon = \mu$), and only the last one needs to be dealt with explicitly, by working it out by parts and then using a table integral:²⁷

$$\int_0^{\infty} (\varepsilon - \mu)^2 \left(-\frac{\partial \langle N_k \rangle}{\partial \varepsilon} \right) d\varepsilon \approx T^2 \int_{-\infty}^{+\infty} \xi^2 \frac{d}{d\xi} \left(-\frac{1}{e^{\xi} + 1} \right) d\xi = 4T^2 \int_0^{+\infty} \frac{\xi d\xi}{e^{\xi} + 1} = 4T^2 \frac{\pi^2}{12}. \quad (3.63)$$

Being plugged into Eq. (62), this result proves the Sommerfeld formula (59).

The last preparatory step we need is to take into account a possible small difference (as we will see below, also proportional to T^2) between the temperature-dependent chemical potential $\mu(T)$ and the Fermi energy defined as $\varepsilon_F \equiv \mu(0)$, in the largest (first) term in the right-hand part of Eq. (62), to write

$$I(T) \approx \int_0^{\varepsilon_F} \varphi(\varepsilon) d\varepsilon + (\mu - \varepsilon_F) \varphi(\mu) + \frac{\pi^2}{6} T^2 \frac{d\varphi(\mu)}{d\mu} = I(0) + (\mu - \varepsilon_F) \varphi(\mu) + \frac{\pi^2}{6} T^2 \frac{d\varphi(\mu)}{d\mu}. \quad (3.64)$$

Now, applying this formula to Eq. (42) and the last form of Eq. (52), we get the following results (which are valid for any dispersion law $\varepsilon(\mathbf{p})$ and even any dimensionality of the gas):

$$N(T) = N(0) + (\mu - \varepsilon_F) g(\mu) + \frac{\pi^2}{6} T^2 \frac{dg(\mu)}{d\mu}, \quad (3.65)$$

$$E(T) = E(0) + (\mu - \varepsilon_F) \mu g(\mu) + \frac{\pi^2}{6} T^2 \frac{d}{d\mu} [\mu g(\mu)]. \quad (3.66)$$

However, the number of particles does not change with temperature, $N(T) = N(0)$, so that Eq. (65) gives an equation for finding the temperature-induced change of μ :

$$\mu - \varepsilon_F = -\frac{\pi^2}{6} T^2 \frac{1}{g(\mu)} \frac{dg(\mu)}{d\mu}. \quad (3.67)$$

Note that the change is quadratic in T and negative, in agreement with the numerical results shown in Fig. 1a. Plugging this expression (which is only valid when the magnitude of the change is much smaller than ε_F) into Eq. (66), we finally get the finite-temperature correction to energy:

$$E(T) - E(0) = \frac{\pi^2}{6} g(\mu) T^2, \quad (3.68)$$

where within the accuracy of our approximation, μ may be replaced with ε_F . (Due to the universal relation (48), Eq. (68) also gives the temperature correction to pressure.) Now we may use Eq. (68) to calculate the heat capacity of the degenerate Fermi gas:

Low- T
heat
capacity

$$C_V \equiv \left(\frac{\partial E}{\partial T} \right)_V = \gamma T, \quad \gamma = \frac{\pi^2}{3} g(\varepsilon_F). \quad (3.69)$$

According to Eq. (55b), in the particular case of a 3D gas with the isotropic and parabolic dispersion law (3), Eq. (69) reduces to

²⁷ See, e.g., MA Eqs. (6.8c) and (2.12b), with $n = 1$.

$$\gamma = \frac{\pi^2}{2} \frac{N}{\varepsilon_F}, \quad \text{i.e. } C_V = \frac{\pi^2}{2} N \frac{T}{\varepsilon_F} \ll N. \quad (3.70)$$

This important result deserves a discussion. First, note that within the range of validity of the Sommerfeld approximation ($T \ll \varepsilon_F$), the specific heat of the degenerate gas is much smaller than that of the classical gas, even without internal degrees of freedom, $C_V = (3/2)N$ – see Eq. (19). The reason for such a small heat capacity is that particles deep inside the Fermi sea cannot pick up thermal excitations with available energies of the order of $T \ll \varepsilon_F$, because all states around them are already occupied. The only particles (or rather quantum states) that may be excited with such small energies are those at the very Fermi surface, more exactly within a surface layer of thickness $\Delta\varepsilon \sim T \ll \varepsilon_F$, and Eq. (69) presents a very vivid expression of this fact.

The second important feature of Eqs. (69)-(70) is the linear dependence of the heat capacity on temperature, which decreases with a reduction of T much slower than that of crystal vibrations – see Eq. (2.99) and its discussion. This means that in metals the specific heat at temperatures $T \ll T_D$ is dominated by the conduction electrons. Indeed, experiments confirm not only the linear dependence (70) of the specific heat,²⁸ but also the values of the proportionality coefficient $\gamma \equiv C_V/T$ for cases when ε_F can be calculated independently, for example for alkali metals – see the right two columns of Table 1. More typically, Eq. (69) is used for the experimental measurement of the density of states on the Fermi surface, $g(\varepsilon_F)$ – the factor which participates in many theoretical results, in particular in transport properties of degenerate Fermi gases (see Chapter 6 below).

3.4. Bose-Einstein condensation

Now let us explore what happens at cooling of an ideal gas of bosons. Figure 3a shows on a more appropriate, log-log scale, the same plot as Fig. 1b, i.e. the numerical solution of Eq. (47) with the appropriate (negative) sign in the denominator. One can see that the chemical potential μ indeed tends to zero at some finite “critical temperature” T_c . This temperature may be found by taking $\mu = 0$ in Eq. (47), which is then reduced to a table integral:²⁹

$$T_c = T_0 \left[\frac{1}{\sqrt{2\pi^2}} \int_0^\infty \frac{\xi^{1/2} d\xi}{e^\xi - 1} \right]^{-2/3} = T_0 \left[\frac{1}{\sqrt{2\pi^2}} \Gamma\left(\frac{3}{2}\right) \zeta\left(\frac{3}{2}\right) \right]^{-2/3} \approx 3.313 T_0, \quad (3.71) \quad \text{Critical temperature}$$

the result explaining the T_c/T_0 ratio mentioned in Sec. 2.

Hence we must have a good look at the temperature interval $0 < T < T_c$, which may look rather mysterious. Indeed, within this range, chemical potential μ cannot be either negative or zero, because then Eq. (41) would give a value of N fewer than the number of particles we actually have. On the other hand, μ cannot be positive either, because integral (41) would diverge at $\varepsilon \rightarrow \mu$ due to the divergence of $\langle N(\varepsilon) \rangle$ – see, e.g., Fig. 2.15. The only possible resolution of the paradox, suggested by A. Einstein, is as follows: at $T < T_c$, the chemical potential of each particle still equals exactly zero, but a certain number

²⁸ Solids, with their low thermal expansion coefficients, present a virtually fixed-volume confinement for the electron gas, so that the specific heat measured at ambient conditions may be legitimately compared with calculated c_V .

²⁹ See, e.g., MA Eqs. (6.8b) and (6.6c) with $s = 3/2$.

(N_0 of N) of them are in the ground state (with $\varepsilon \equiv p^2/2m = 0$), forming the so-called *Bose-Einstein condensate*, very frequently referred to as BEC.

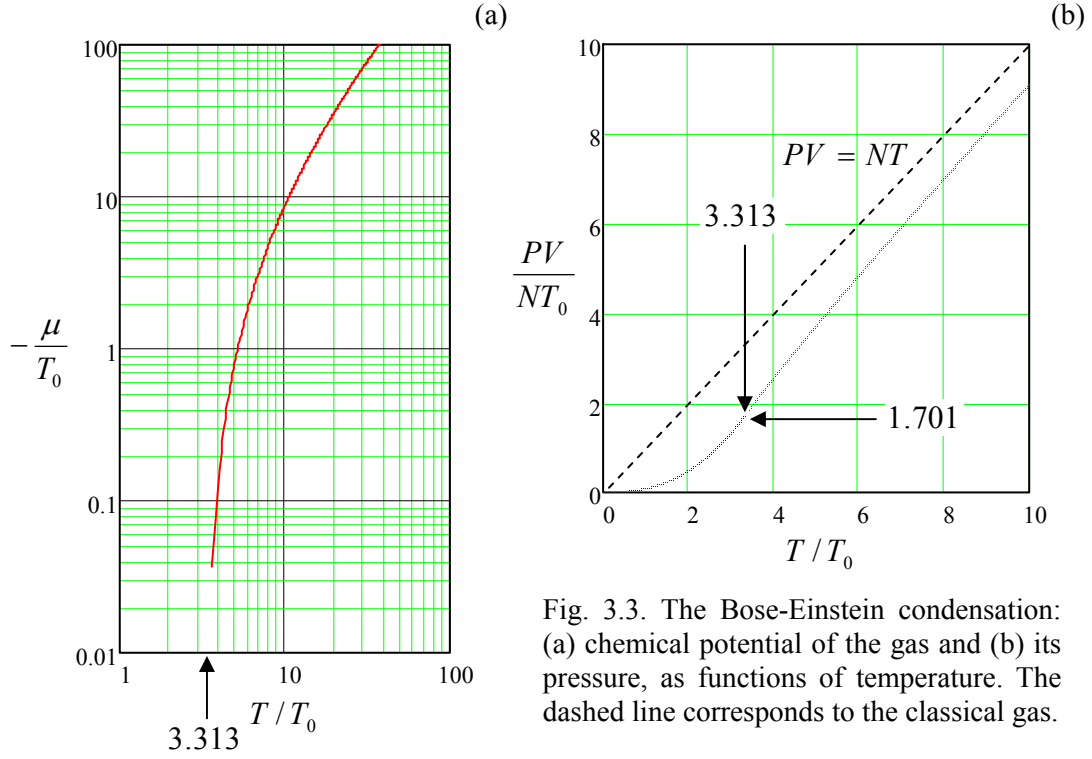


Fig. 3.3. The Bose-Einstein condensation: (a) chemical potential of the gas and (b) its pressure, as functions of temperature. The dashed line corresponds to the classical gas.

Since the condensate particles do not contribute to Eq. (41) (because of the factor $\varepsilon^{1/2} = 0$), their number N_0 may be calculated by using Eq. (44), with $\mu = 0$, to find the number ($N - N_0$) of particles still remaining in the gas, i.e. having energy $\varepsilon > 0$:

$$N - N_0 = \frac{gV(mT)^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \frac{\xi^{1/2} d\xi}{e^\xi - 1}. \quad (3.72)$$

This result is even simpler than it may look. Indeed, let us write it for case $T = T_c$, when $N_0 = 0$:³⁰

$$N = \frac{gV(mT_c)^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \frac{\xi^{1/2} d\xi}{e^\xi - 1}. \quad (3.73)$$

Since the dimensionless integrals in both equations are similar, we may just divide them, getting an extremely simple and elegant result:

$$\frac{N - N_0}{N} = \left(\frac{T}{T_c}\right)^{3/2}, \quad \text{so that} \quad N_0 = N \left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right], \quad \text{at } T \leq T_c. \quad (3.74a)$$

Please note that this result is only valid for the particles whose motion, within volume V , is free – in other words, for the particles trapped in a rigid-wall box of volume V . In typical experiments with the Bose-Einstein condensation of diluted gases of neutral (and hence weakly interacting) atoms, particles

³⁰ This is, of course, just another form of Eq. (71).

are trapped at the bottom of a “soft” potential well, which may be well approximated by a 3D quadratic parabola: $U(\mathbf{r}) = m\omega^2 r^2/2$. It is straightforward to show (and hence left for reader’s exercise) that in this case the temperature dependence of N_0 is somewhat different:

$$N_0 = N \left[1 - \left(\frac{T}{T_c^*} \right)^3 \right], \quad \text{at } T \leq T_c^*, \quad (3.74b)$$

where T_c^* is a critical temperature that depends on $\hbar\omega$, i.e. the confining potential’s “steepness”, rather than on the gas’ volume (which in this case is not fixed). Figure 4 shows one of the first sets of experimental data for the Bose-Einstein condensation of dilute gases of neutral atoms. Taking into account the finite number of particles in the experiment, the agreement with the simple theory is surprisingly good.

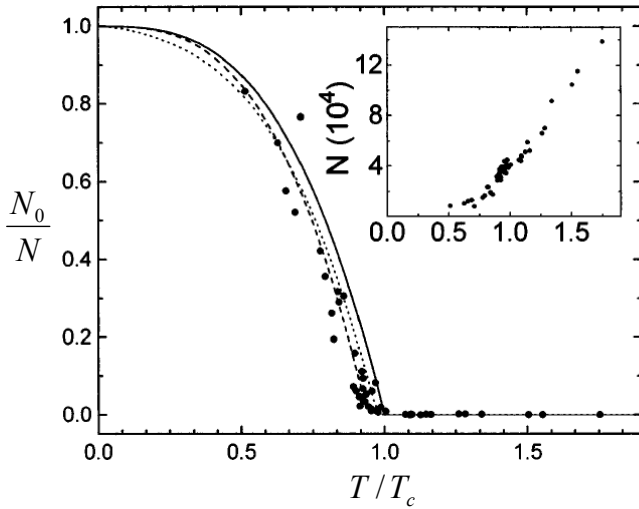


Fig. 3.4. Total number N of trapped ^{87}Rb atoms (inset) and their ground-state fraction N_0/N , as functions of the ratio T/T_c , as measured by J. Ensher *et al.*, *Phys. Rev. Lett.* **77**, 4984 (1996). In this experiment, T_c^* was as low as 0.28×10^{-6} K. The solid line shows the simple theoretical dependence $N(T)$, given by Eq. (74b), while other lines correspond to more complex theories taking into account the finite number N of trapped atoms. © 1996 APS.

Now returning to the rigid-wall box model, let us explore what happens at the critical temperature and below it with other gas parameters. Equation (52) with the appropriate (lower) sign shows that approaching this point from higher temperatures, gas energy and hence its pressure do not vanish (Fig. 3b). Indeed, at $T = T_c$ (where $\mu = 0$), that equation yields³¹

$$E(T_c) = gV \frac{m^{3/2} T_c^{5/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\infty \frac{\xi^{3/2} d\xi}{e^\xi - 1} = gV \frac{m^{3/2} T_c^{5/2}}{\sqrt{2\pi^2 \hbar^3}} \Gamma\left(\frac{5}{2}\right) \zeta\left(\frac{5}{2}\right) = \frac{3}{2} \frac{\zeta(5/2)}{\zeta(3/2)} NT_c \approx 0.7701 NT_c, \quad (3.75)$$

so that using the universal relation (48), we get a pressure value,

$$P(T_c) = \frac{2}{3} \frac{E(T_c)}{V} = \frac{\zeta(5/2)}{\zeta(3/2)} \frac{N}{V} T_c \approx 0.5134 \frac{N}{V} T_c \approx 1.701 P_0, \quad (3.76)$$

which is somewhat lower than, but comparable to $P(0)$ for the fermions – cf. Eq. (57). Now we can use the same Eq. (52), also with $\mu = 0$, to calculate the energy of the gas at $T < T_c$,

³¹ For the involved dimensionless integral see, e.g., MA Eqs. (6.8b) and (6.6c) with $s = 5/2$.

$$E(T) = gV \frac{m^{3/2} T^{5/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\xi^{3/2} d\xi}{e^\xi - 1}. \quad (3.77)$$

Comparing this relation with the first form of Eq. (75), which features the same integral, we immediately get one more simple temperature dependence:

BEC:
energy
below T_c

$$E(T) = E(T_c) \left(\frac{T}{T_c} \right)^{5/2}, \quad \text{at } T \leq T_c. \quad (3.78)$$

From the universal relation (44), we immediately see that pressure follows the same dependence:

BEC:
pressure
below T_c

$$P(T) = P(T_c) \left(\frac{T}{T_c} \right)^{5/2}, \quad \text{at } T \leq T_c. \quad (3.79)$$

This temperature dependence of pressure is shown with the blue line in Fig. 3b. The plot shows that for all temperatures (both below and above T_c) the pressure of bosonic gas is below that of the classical gas of the same density. Note also that since, according to Eqs. (57) and (76), $P(T_c) \propto P_0 \propto V^{-5/3}$, while, according to Eqs. (37) and (71), $T_c \propto T_0 \propto V^{-2/3}$, pressure (79) does not depend on volume at all! The physics of this result (that is valid at $T < T_c$ only) is that as we decrease the volume at fixed total number of particles, more and more of them go to the condensate, decreasing the number ($N - N_0$) of particles in the gas phase, but not changing its pressure. Such behavior is very typical for phase transitions – see, in particular, the next chapter.

The last thermodynamic variable of major interest is the heat capacity, because it may be readily measured in many systems. For temperatures $T \leq T_c$, it may be easily calculated from Eq. (78):

$$C_V(T) \equiv \left(\frac{\partial E}{\partial T} \right)_{N,V} = E(T_c) \frac{5}{2} \frac{T^{3/2}}{T_c^{5/2}}, \quad (3.80)$$

so that below T_c , the capacity *increases*, at the critical temperature reaching the value,

$$C_V(T_c) = \frac{5}{2} \frac{E(T_c)}{T_c} \approx 1.925 N, \quad (3.81)$$

which is approximately 28% above that ($3N/2$) of the classical gas - in both cases ignoring the possible contributions from the internal degrees of freedom. The analysis for $T \geq T_c$ is a little bit more cumbersome, because differentiating E over temperature - say, using Eq. (52) - one should also take into account the temperature dependence of μ that follows from Eq. (40) – see also Fig. 1b. However, the most important feature of the result may be predicted without the calculation (which is being left for reader's exercise). Since at $T \gg T_c$ the heat capacity has to approach the classical value, it must *decrease* at $T > T_c$, thus forming a sharp maximum (a “cusp”) at the critical point $T = T_c$ – see Fig. 5.

Such a cusp is good indication of the Bose-Einstein condensation in virtually any experimental system, especially because inter-particle interactions (unaccounted for in our simple discussion) typically make this feature even more substantial, turning it into a weak (logarithmic) singularity. Historically, such a singularity (called the λ -point because of the characteristic shape of the $C_V(T)$ dependence) was the first noticed, though not immediately understood sign of the Bose-Einstein condensation, observed in 1931 by W. Keesom and K. Clusius in liquid ^4He at $T = T_c \approx 2.17 \text{ K}$. Other milestones of the Bose-Einstein condensation studies include:

- the experimental discovery of superconductivity in metals, by H. Kamerlingh-Onnes in 1911;
- the development of the Bose-Einstein statistics implying the condensation, in 1924-1925;
- the discovery of superfluidity in liquid ^4He by P. Kapitza and (independently) by J. Allen and D. Misener in 1937, and its explanation as a result of the Bose-Einstein condensation by F. and H. Londons and L. Titz, with further elaborations by L. Landau (all in 1938);
- the explanation of superconductivity as the result of formation of *Cooper pairs* of electrons, with an integer total spin, with the simultaneous Bose-Einstein condensation of such effective bosons, by J. Bardeen, L. Cooper, and J. Schrieffer in 1957;
- the discovery of superfluidity of two different phases of ^3He , due to the similar Bose-Einstein condensation of pairs of its fermion atoms, by D. Lee, D. Osheroff, and R. Richardson in 1972;
- the first observation of the Bose-Einstein condensation in dilute gases (^{87}Ru by E. Cornell, C. Wieman *et al.* and ^{23}Na by W. Ketterle *et al.*) in 1995.

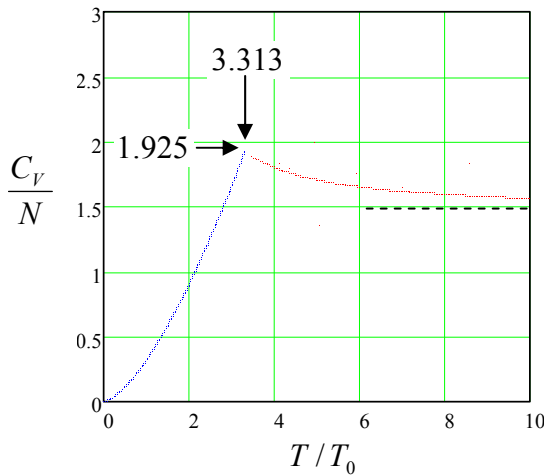


Fig. 3.5. Temperature dependences of the heat capacity of an ideal Bose-Einstein gas, calculated from Eqs. (52) and (40) for $T \geq T_c$, and from Eq. (80) for $T \leq T_c$.

The importance of the last achievement (and of the continuing intensive work in this direction³²) stems from the fact that in contrast to other Bose-Einstein condensates, in dilute gases (with the typical density n as low as $\sim 10^{14} \text{ cm}^{-3}$) the particles interact very weakly, and hence many experimental results are very close to the simple theory described above and its straightforward elaborations - see, e.g., Fig. 4. On the other hand, the importance of prior implementations of the Bose-Einstein condensates, which involve more complex and challenging physics, should not be underestimated - as it sometimes is.

The most important feature of any Bose-Einstein condensate is that all N_0 condensed particles are in the same quantum state, and hence are described by exactly the same wavefunction. This wavefunction is substantially less “feeble” than that of a single particle - in the following sense. In the second quantization language,³³ the well-known Heisenberg’s uncertainty relation may be rewritten for the creation/annihilation operators; in particular, for bosons,

$$[\hat{a}, \hat{a}^\dagger] = 1. \quad (3.82)$$

³² Its detailed discussion may be found, e.g., in: C. Pethick and H. Smith, *Bose-Einstein Condensation in Dilute Gases*, 2nd ed., Cambridge U. Press, 2008.

³³ See, e.g., QM Sec. 8.3.

Since $\hat{a}$ and $\hat{a}^\dagger$ are quantum-mechanical operators of the complex amplitude $a = A\exp\{i\varphi\}$ and its complex conjugate $a^* = A\exp\{-i\varphi\}$, where A and φ are real amplitude and phase of the wavefunction. Equation (82) yields the following approximate uncertainty relation (strict in the limit $\delta\varphi \ll 1$) between the number of particles $N = AA^*$ and phase φ

$$\delta N \delta\varphi \geq 1/2. \quad (3.83)$$

This means that a condensate of $N \gg 1$ bosons may be in a state with both phase and amplitude of the wavefunction behaving virtually as c -numbers, with negligible relative uncertainties: $\delta N \ll N$, $\delta\varphi \ll 1$. Moreover, such states are much less susceptible to perturbations by experimental instruments. For example, the *supercurrent* I_s carried along a superconducting wires by a coherent Bose-Einstein condensate of Cooper pairs may be as high as hundreds of amperes. As a result, the “strange” behaviors predicted by the quantum mechanics are not averaged out as in the usual particle ensembles (see, e.g., the discussion of the density matrix in Sec. 2.1), but may be directly revealed in macroscopic, measurable behaviors of the condensate.

For example, density $\mathbf{j}_s$ of the supercurrent may be described by the same formula as the usual probability current density of a single particle,³⁴ multiplied by the Cooper pair density n and the electric charge $q = -2e$ of a single pair:

$$\mathbf{j}_s = qn \frac{\hbar}{m} \left(\nabla\varphi - \frac{q}{\hbar} \mathbf{A} \right), \quad (3.84)$$

where $\mathbf{A}$ is the vector-potential of the (electro)magnetic field. If a superconducting wire is not extremely thin, current flow does not penetrate its interior,³⁵ so that $\mathbf{j}_s$ may be taken for zero. As a result, the integral of Eq. (84), taken along a contour inside a closed wire loop yields

$$\frac{q}{\hbar} \oint_C \mathbf{A} \cdot d\mathbf{r} = \Delta\varphi = 2\pi m, \quad (3.85)$$

where m is an integer. But, according to electrodynamics, the integral participating in this equation is nothing more than flux Φ of the magnetic field $\mathcal{B}$ piercing the wire loop area A . Thus we immediately arrive at the famous *magnetic flux quantization effect*

$$\Phi \equiv \int_A \mathcal{B}_n d^2r = m\Phi_0, \quad \Phi_0 \equiv \frac{2\pi\hbar}{|q|} = \frac{h}{2e} \approx 2.07 \times 10^{-15} \text{ Wb}, \quad (3.86)$$

which was theoretically predicted in 1950 and experimentally observed in 1961. Most fantastically, this effect holds true even in very large loops, sustained by the Bose-Einstein condensate of Cooper pairs, “coherent over miles of dirty lead wire”, citing J. Bardeen’s famous expression.

Other prominent examples of such *macroscopic quantum effects* in Bose-Einstein condensates include not only the superfluidity and superconductivity as such, but also the Josephson effect,

³⁴ See, e.g., QM Eq. (3.28).

³⁵ This is the *Meissner-Ochsenfeld* (or just “Meissner”) effect which may be also readily explained using Eq. (84), combined with the Maxwell equations – see, e.g., EM Sec. 6.3.

quantized Abrikosov vortices, etc. Some of these effects are briefly discussed in other parts of this series.³⁶

3.5. Gases of weakly interacting particles

Now let us discuss the weak particle interaction effects on macroscopic properties of their gas. (Unfortunately, I will have time to do that only for a brief discussion of these effects in classical gases of indistinguishable particles.³⁷)

In most cases of interest, particle interaction may be described by certain potential energy U , so that the total energy is

$$E = \sum_{k=1}^N \frac{p_k^2}{2m} + U(\mathbf{r}_1, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N), \quad (3.87)$$

where $\mathbf{r}_k$ is the position of k^{th} particle's center. Let us see how far would the statistical physics allow us to proceed for an arbitrary potential U . For $N \gg 1$, at the calculation of the Gibbs statistical sum (2.59), we may perform the usual transfer from the summation over all quantum states of the system to integration over the $6N$ -dimensional space, with the correct Boltzmann counting:

$$\begin{aligned} Z &= \sum_m e^{-E_m/T} \rightarrow \frac{1}{N!} \frac{g^N}{(2\pi\hbar)^{3N}} \int \exp\left\{-\sum_{k=1}^N \frac{p_k^2}{2mT}\right\} d^3 p_1 \dots d^3 p_N \int \exp\left\{-\frac{U(\mathbf{r}_1, \dots, \mathbf{r}_N)}{T}\right\} d^3 r_1 \dots d^3 r_N \\ &= \left(\frac{1}{N!} \frac{g^N V^N}{(2\pi\hbar)^{3N}} \int \exp\left\{-\sum_{k=1}^N \frac{p_k^2}{2mT}\right\} d^3 p_1 \dots d^3 p_N \right) \times \left(\frac{1}{V^N} \int \exp\left\{-\frac{U(\mathbf{r}_1, \dots, \mathbf{r}_N)}{T}\right\} d^3 r_1 \dots d^3 r_N \right). \end{aligned} \quad (3.88)$$

But according to Eq. (14), the first operand in the last product is the statistical sum of an ideal gas (with the same g , N , V , and T), so that we may use Eq. (2.63) to write

$$F = F_{\text{ideal}} - T \ln \left[\frac{1}{V^N} \int d^3 r_1 \dots d^3 r_N e^{-U/T} \right] = F_{\text{ideal}} - T \ln \left[1 + \frac{1}{V^N} \int d^3 r_1 \dots d^3 r_N (e^{-U/T} - 1) \right], \quad (3.89)$$

where F_{ideal} is the free energy of the ideal gas (i.e. the same gas but with $U = 0$), given by Eq. (16).

I believe that Eq. (89) is a very convincing demonstration of the enormous power of the statistical physics. Instead of trying to solve an impossibly complex problem of classical dynamics of $N \gg 1$ (think of $N \sim 10^{23}$) interacting particles, and calculating appropriate ensemble averages later on, the Gibbs approach reduces finding the free energy (and then, from thermodynamic relations, all other thermodynamic variables) to the calculation of just one integral in its right-hand part of Eq. (89). Still, this integral is $3N$ -dimensional and may be worked out analytically only if particle interaction is weak in some sense. Indeed, the last form of Eq. (89) makes it especially evident that if $U \rightarrow 0$ everywhere, the term in parentheses under the integral vanishes, and so does the integral itself, and hence the addition to F_{ideal} .

³⁶ See QM Sec. 2.3, and EM Secs. 6.3 and 6.4. Recently, some of these effects were observed in the Bose-Einstein condensates of diluted gases as well.

³⁷ A concise discussion of weak interactions in *quantum* gases may be found, for example, in Chapter 10 of K. Huang, *Statistical Mechanics*, 2nd ed., Wiley, 2003.

Now let us see what would this integral yield for the simplest, *short-range* interactions, in which potential U is substantial only when the mutual distance $\mathbf{r}_{jj'} \equiv \mathbf{r}_j - \mathbf{r}_{j'}$ between particle centers is smaller than certain value $2r_0$, where r_0 may be interpreted as the particle size scale. If the gas is sufficiently dilute, so that the particle radius r_0 is much smaller than the average distance r_A between the particles, the integral in Eq. (89) is of the order of $(2r_0)^{3N}$, i.e. much smaller than $r_A^{3N} \sim V^N$. Then we may expand the logarithm in Eq. (89) into the Taylor series with respect to the small second term in the square brackets, and keep just the first term of the series:

$$F \approx F_{\text{ideal}} - \frac{T}{V^N} \int d^3 r_1 \dots d^3 r_N (e^{-U/T} - 1). \quad (3.90)$$

Even more importantly, if the gas density is so low that the chances for 3 or more particles to come close to each other and interact (collide) are very small, *pair collisions* are the most important. In this case, we may recast the integral in Eq. (90) as a sum of $N(N-1)/2 \approx N^2/2$ similar terms describing such pair interactions, each of the type

$$V^{N-2} \int (e^{-U(\mathbf{r}_{kk'})/T} - 1) d^3 r_k d^3 r_{k'}. \quad (3.91)$$

It is convenient to think about $\mathbf{r}_{kk'}$ as the radius-vector of particle k in the reference frame with the origin placed at particle k' – see Fig. 6a.

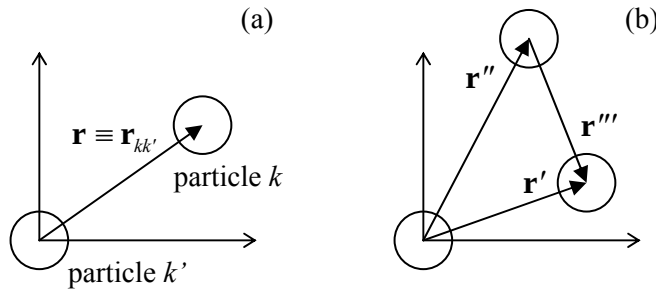


Fig. 3.6. The definition of interparticle distance vectors at their (a) pair and (b) triple interactions.

Then it is clear that in Eq. (91), we may first calculate the integral over $\mathbf{r}_k$ while keeping the distance vector $\mathbf{r}_{kk'}$, and hence $U(\mathbf{r}_{kk'})$, constant, getting one more factor V . Moreover, since all particle pairs are similar, in the remaining integral over $\mathbf{r}_{kk'}$ we may drop the radius-vector index, so that Eq. (90) becomes

$$F = F_{\text{ideal}} - \frac{T}{V^N} \frac{N^2}{2} V^{N-1} \int (e^{-U(\mathbf{r})/T} - 1) d^3 r = F_{\text{ideal}} + \frac{T}{V} N^2 B(T), \quad (3.92)$$

where $B(T)$, called the *second virial coefficient*,³⁸ has an especially simple form for spherically-symmetric interactions:

³⁸ Term “virial”, from Latin *viris* (meaning “force”), was introduced to molecular physics by R. Clausius. The motivation for adjective “second” for $B(T)$ is evident from the last form of Eq. (94), with the “first virial coefficient”, standing before the N/V ratio and sometimes denoted $A(T)$, equal to 1 – see also Eq. (100) below.

$$B(T) \equiv \frac{1}{2} \int (1 - e^{-U(\mathbf{r})/T}) d^3r \rightarrow \frac{1}{2} \int_0^\infty 4\pi r^2 dr (1 - e^{-U(r)/T}). \quad (3.93)$$

Second
virial
coefficient

From Eq. (92), and the second of the thermodynamic relations (1.35), we already can already tell something important about the equation of state:

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = P_{\text{ideal}} + \frac{N^2 T}{V^2} B(T) = T \left[\frac{N}{V} + B(T) \frac{N^2}{V^2} \right]. \quad (3.94)$$

We see that at a fixed gas density $n = N/V$, the pair interaction creates additional pressure, proportional to $(N/V)^2 = n^2$ and a function of temperature, $B(T)T$.

Let us calculate $B(T)$ for a couple of simple models of particle interactions. Solid line in Fig. 7 shows (schematically) a typical form of the interaction potential between electrically neutral molecules with zero spontaneous electric dipole momentum.

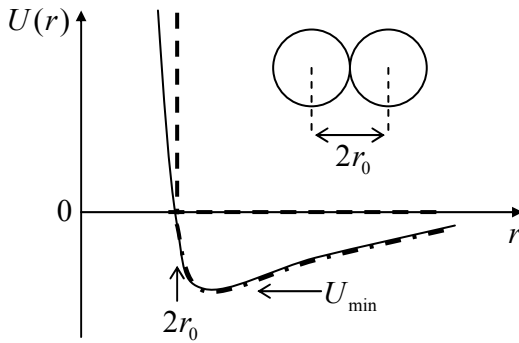


Fig. 3.7. Pair interaction of particles. Solid line: a typical interaction potential; dashed line: its hardball model (95); dash-dotted line: the improved model (97) – schematically. The inset illustrates the idea of the hardball model.

At large distances the interaction of particles that do not have their own permanent electrical dipole moment $\mathbf{p}$, is dominated by the attraction (the so-called *London dispersion force*) between correlated components of the spontaneously induced dipole moments, giving $U(r) \rightarrow r^{-6}$ at $r \rightarrow \infty$.³⁹ At closer distances the potential is always repulsive ($U > 0$) and growing very fast at $r \rightarrow 0$, but its quantitative form is specific for each particular molecule.⁴⁰ The crudest description of such repulsion is given by the so-called *hardball model*:

³⁹ Indeed, the independent fluctuation-induced components $\mathbf{p}(t)$ and $\mathbf{p}'(t)$ of dipole moments of two particles have random mutual orientation, so that the time average of their interaction energy, proportional to r^{-3} , vanishes. However, the electric field $\mathcal{E}$ of each dipole $\mathbf{p}$, proportional as r^{-3} , induces a correlated component of $\mathbf{p}'$, also proportional to r^{-3} , giving a potential energy of their interaction, proportional to $\mathbf{p}' \cdot \mathcal{E} \propto r^{-6}$, with a non-vanishing time average. A detailed theory of this effect, closely related to the Casimir effect in quantum mechanics (see, e.g., QM Sec. 9.1) may be found, e.g., in Secs. 80-82 of E. Lifshitz and L. Pitaevskii, *Statistical Mechanics*, pt. 2, Pergamon, 1980.

⁴⁰ Note that the particular form of the first term in the approximation $U(r) = a/r^{12} - b/r^6$ (called the *Lennard-Jones potential* or the “12-6 potential”), suggested in 1924, lacks physical justification and was soon replaced, in professional physics, by better approximations, including the so-called *exp-6 model* (better fitting most experimental data) and the *Morse potential* (more convenient for quantum-mechanical calculations – see QM Chapter 2). However, the Lennard-Jones potential still travels from one undergraduate textbook to another, as a trick for simpler calculation of the equilibrium distance between the particles by differentiation.

$$U(r) = \begin{cases} +\infty, & \text{for } 0 < r < 2r_0, \\ 0, & \text{for } 2r_0 < r < \infty, \end{cases} \quad (3.95)$$

- see the dashed line and inset in Fig. 7. According to Eq. (93), in this model the second virial coefficient is temperature-independent:

$$B(T) = b \equiv \frac{1}{2} \int_0^{2r_0} 4\pi r^2 dr = \frac{2\pi}{3} (2r_0)^3, \quad (3.96)$$

(and is 4 times larger than the hardball volume $V_0 = (4\pi/3)r_0^3$), so that the equation of state (94) still gives a linear dependence of pressure on temperature.

A correction to this result may be obtained by the following approximate account of the long-range attraction (see the dash-dotted line in Fig. 7):⁴¹

$$U(r) = \begin{cases} +\infty, & \text{for } 0 < r < 2r_0, \\ U(r), & \text{with } |U| \ll T, \text{ for } 2r_0 < r < \infty, \end{cases} \quad (3.97)$$

which is sometimes called the *hard core model*. Then Eq. (93) yields:

$$B(T) = b + \frac{1}{2} \int_{2r_0}^{\infty} 4\pi r^2 dr \frac{U(r)}{T} = b - \frac{a}{T}, \quad \text{with } a \equiv 2\pi \int_{2r_0}^{\infty} r^2 dr |U(r)|. \quad (3.98)$$

In this model, the equation of state (94) acquires a temperature-independent term:

$$P = T \left[\frac{N}{V} + \left(\frac{N}{V} \right)^2 \left(b - \frac{a}{T} \right) \right]. \quad (3.99)$$

Still, the correction to the ideal-gas pressure is proportional to $(N/V)^2$, and has to be relatively small for Eq. (99) to be valid, so that the right-hand part of Eq. (99) may be considered as the sum of two leading terms in the general expansion of P into the Taylor series in low density $n = N/V$ of the gas:

$$P = T \left[\frac{N}{V} + B(T) \left(\frac{N}{V} \right)^2 + C(T) \left(\frac{N}{V} \right)^3 + \dots \right], \quad (3.100)$$

where $C(T)$ is called the *third virial coefficient*. It is natural to ask how can we calculate $C(T)$ and the higher virial coefficients.

Generally, this may be done just by a careful analysis of Eq. (90),⁴² but I would like to use this occasion to demonstrate a different, very interesting approach, called the *cluster expansion method*,⁴³

⁴¹ The strong inequality between U and T in this model is necessary not only to make calculations simpler. A deeper reason is that if $(-U_{\min})$ becomes comparable with, or larger than T , particles may become trapped in the potential well formed by this potential, forming a different phase – a liquid or a solid. In such phases, the probability to find more than two particles interacting simultaneously is high, so that approximation (92), on which all our further results are based, becomes invalid.

⁴² L. Boltzmann has used that way to calculate the 3rd and 4th virial coefficients for the hardball model – as much as can be done analytically.

which allows to streamline such calculations. Let us apply to our system, with energy (87), the grand canonical distribution. (Just as in Sec. 2, we may argue that if the average number $\langle N \rangle$ of particles in a member of a grand canonical ensemble, with fixed μ and T , is much larger than 1, the relative fluctuations of that number are small, so that all its thermodynamic properties should be similar to those when N is exactly fixed - as it is assumed when applying the Gibbs distribution valid for the canonical ensemble.) For our case, the grand canonical distribution, Eq. (2.109), may be recast as

$$\Omega = -T \ln \sum_{N=0}^{\infty} Z_N, \quad Z_N \equiv e^{\mu N/T} \sum_m e^{-E_{m,N}/T}, \quad E_{m,N} = \sum_{k=1}^N \frac{p_k^2}{2m} + U(r_1, \dots, r_N). \quad (3.101)$$

(Notice that here, as always in the grand canonical distribution, N means a particular rather than average number of particles.) Now, let us try to forget for a second that in real systems of interest the number of particles is extremely large, and start to calculate, one by one, the first terms Z_N .

In the term with $N = 0$, both contributions to $E_{m,N}$ vanish, and so does $\mu N/T$, so that $Z_0 = 1$. In the next term, with $N = 1$, the interaction term vanishes, so that $E_{m,1}$ is reduced to kinetic energy of one particle, giving

$$Z_1 = e^{\mu/T} \sum_k \exp \left\{ -\frac{p_k^2}{2mT} \right\}. \quad (3.102)$$

Making the usual transition from summation to integration, we may write

$$Z_1 = Z I_1, \quad \text{where } Z \equiv e^{\mu/T} \frac{gV}{(2\pi\hbar)^3} \int \exp \left\{ -\frac{p^2}{2mT} \right\} d^3 p, \quad \text{and } I_1 \equiv 1. \quad (3.103)$$

This is the same simple (Gaussian) integral as in Eq. (6), giving

$$Z = e^{\mu/T} \frac{gV}{(2\pi\hbar)^3} (2\pi mT)^{3/2} = e^{\mu/T} gV \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2}. \quad (3.104)$$

Now let us explore the next term, with $N = 2$, which describes, in particular, pair interactions $U = U(\mathbf{r})$, with $\mathbf{r} = \mathbf{r}' - \mathbf{r}''$. Due to the particle indistinguishability, this term needs the “correct Boltzmann counting” factor $1/2!$ – cf. Eqs. (12) and (88):

$$Z_2 = e^{2\mu/T} \frac{1}{2!} \sum_{k,k'} \left(\exp \left\{ -\frac{p_k^2}{2mT} - \frac{p_{k'}^2}{2mT} \right\} e^{-U(\mathbf{r})/T} \right). \quad (3.105)$$

Since U is coordinate-dependent, here the transfer from summation to integration should be done more carefully than in the first term – cf. Eqs. (24) and (88):

$$Z_2 = e^{2\mu/T} \frac{1}{2!} \frac{(gV)^2}{(2\pi\hbar)^6} \int \exp \left\{ -\frac{p^2}{2mT} \right\} d^3 p \int \exp \left\{ -\frac{p'^2}{2mT} \right\} d^3 p' \times \frac{1}{V} \int e^{-U(\mathbf{r})/T} d^3 r. \quad (3.106)$$

Comparing this expression with the definition of parameter Z in Eq. (103), we get

⁴³ This method was developed in 1937-38 by J. Mayer and collaborators for a classical gas, and generalized to quantum systems in 1938 by B. Kahn and G. Uhlenbeck.

$$Z_2 = \frac{Z^2}{2!} I_2, \quad \text{where } I_2 \equiv \frac{1}{V} \int e^{-U(\mathbf{r})/T} d^3r. \quad (3.107)$$

Acting absolutely similarly, for the third term of the grand canonical sum we may get

$$Z_3 = \frac{Z^3}{3!} I_3, \quad I_3 \equiv \frac{1}{V^2} \int e^{-U(\mathbf{r}', \mathbf{r}'')/T} d^3r' d^3r'', \quad (3.108)$$

where $\mathbf{r}'$ and $\mathbf{r}''$ are the vectors characterizing the mutual positions of 3 particles – see Fig. 6b.

These result may be extended by induction to an arbitrary N . Plugging the expression for Z_N into Eq. (101) and recalling that $\Omega = -PV$, we get the equation of state of the gas in the form

$$P = \frac{T}{V} \ln \left(1 + ZI_1 + \frac{Z^2}{2!} I_2 + \frac{Z^3}{3!} I_3 + \dots \right). \quad (3.109)$$

As a sanity check, at $U = 0$, all integrals I_N are obviously equal to 1, the expression under the logarithm is just the Taylor expansion of e^Z , giving $P = TZ/V$, and $\Omega = -PV = -TZ$. In this case, according to the last of Eqs. (1.62), the *average* number of particles in the system is $\langle N \rangle = -(\partial\Omega/\partial\mu)_{T,V} = Z$, because since $Z \propto \exp\{\mu/T\}$, $\partial Z/\partial\mu = Z/T$. Thus, we have happily recovered the equation of state of the ideal gas.⁴⁴

Returning to the general case of nonvanishing interactions, let us assume that the logarithm in Eq. (109) may be also presented as a Taylor series in Z :

Cluster
expansion
of pressure

$$P = \frac{T}{V} \sum_{l=1}^{\infty} \frac{J_l}{l!} Z^l. \quad (3.110)$$

(The lower limit of the sum reflects the fact that according to Eq. (109), at $Z = 0$, $P = (T/V) \ln 1 = 0$.) According to Eq. (1.60), this expansion corresponds to the grand potential

$$\Omega = -PV = -T \sum_{l=1}^{\infty} \frac{J_l}{l!} Z^l. \quad (3.111)$$

Again using the last of Eqs. (1.62), we get

Cluster
expansion
of $\langle N \rangle$

$$\langle N \rangle = \sum_{l=1}^{\infty} \frac{J_l}{(l-1)!} Z^{l-1}. \quad (3.112)$$

This equation, for given $\langle N \rangle$, may be used to find Z and hence for the calculation of the equation of state from Eq. (110). The only remaining conceptual action item is to express coefficients J_l via the integrals I_l participating in expansion (109). This may be done using the well-known Taylor expansion of the logarithm function,⁴⁵

⁴⁴ Actually, the fact that in that case $Z = \langle N \rangle$, could have been noted earlier by comparing Eq. (104) with Eq. (39).

⁴⁵ Looking at Eq. (109), one may think that since $\xi = Z + Z^2 I_2/2 + \dots$ is of the order of at least $Z \sim \langle N \rangle \gg 1$, the expansion (113), which converges only if $|\xi| < 1$, is illegitimate. However, the expansion is justified by its result (114), in which the n -th term is of the order of $\langle N \rangle^n (V_0/V)^{n-1}/n!$, so that the series does converge if the gas density is sufficiently low: $\langle N \rangle/V \ll 1/V_0$, i.e. $r_A \gg r_0$. This is the very beauty of the cluster expansion, whose few first terms present a good approximation even for a gas with $\langle N \rangle \gg 1$ particles.

$$\ln(1 + \xi) = \sum_{l=1}^{\infty} (-1)^{l+1} \frac{\xi^l}{l}. \quad (3.113)$$

Using it together with Eq. (109), we get a Taylor series in Z , starting as

$$P = \frac{T}{V} \left(Z + \frac{Z^2}{2!} (I_2 - 1) + \frac{Z^3}{3!} [(I_3 - 1) - 3(I_2 - 1)] + \dots \right). \quad (3.114)$$

Comparing this expression with Eq. (110), we see that

$$\begin{aligned} J_1 &= 1, \\ J_2 &= I_2 - 1 = \frac{1}{V} \int (e^{-U(\mathbf{r})/T} - 1) d^3r, \\ J_3 &= (I_3 - 1) - 3(I_2 - 1) \\ &= \frac{1}{V^2} \int (e^{-U(\mathbf{r}', \mathbf{r}'')/T} - e^{-U(\mathbf{r}')/T} - e^{-U(\mathbf{r}'')/T} - e^{-U(\mathbf{r}''')/T} + 2) d^3r' d^3r'', \end{aligned} \quad (3.115)$$

Leading coefficients of cluster expansion

where $\mathbf{r}''' \equiv \mathbf{r}' - \mathbf{r}''$ - see Fig. 6b. The expression of J_2 , describing the pair interactions of particles, is (within a numerical factor) equal to the second virial coefficient $B(T)$ - see Eq. (93). As a reminder, the subtraction of 1 from integral I_2 in the second of Eqs. (115) makes the contribution of each elementary 3D volume d^3r into integral J_2 nonvanishing only if at this $\mathbf{r}$ two particles interact ($U \neq 0$). Very similarly, in the last of Eqs. (115), the subtraction of three pair-interaction terms from $(I_3 - 1)$ makes the contribution from elementary 6D volume $d^3r' d^3r''$ into integral J_3 finite only if at that mutual location of particles *all three* of them interact simultaneously.

In order to illustrate the cluster expansion method at work, let us eliminate factor Z from the system of equations (110) and (112), keeping (for the sake of simplicity) the terms up to $O(Z^3)$ only, as has been done in Eq. (114):

$$\frac{PV}{T} = J_1 Z + \frac{J_2}{2} Z^2 + \frac{J_3}{6} Z^3 + \dots, \quad (3.116)$$

$$\langle N \rangle = J_1 Z + J_2 Z^2 + \frac{J_3}{2} Z^3 + \dots \quad (3.117)$$

Dividing these two expressions, we get a result,

$$\frac{PV}{\langle N \rangle T} \approx \frac{1 + (J_2 / 2J_1)Z + (J_3 / 6J_1)Z^2}{1 + (J_2 / J_1)Z + (J_3 / 2J_1)Z^2} = 1 - \frac{J_2}{2J_1} Z + \left(\frac{J_2^2}{2J_1^2} - \frac{J_3}{3J_1} \right) Z^2 + \dots, \quad (3.118)$$

which is accurate with to terms $O(Z^2)$. In this approximation, we may use Eq. (117), solved for Z with the same accuracy:

$$Z \approx \langle N \rangle - \frac{J_2}{J_1} \langle N \rangle^2. \quad (3.119)$$

Plugging this expression into Eq. (118), we get expansion (100) with

$$B(T) = -\frac{J_2}{2J_1} V, \quad C(T) = \left(\frac{J_2^2}{J_1^2} - \frac{J_3}{3J_1} \right) V^2. \quad (3.120)$$

2nd and 3rd virial coefficients

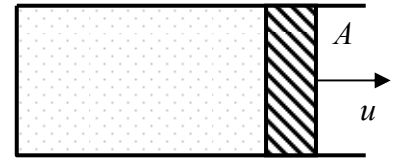
The first of these relations, combined with the first two of Eqs. (115), yields, for the 2nd virial coefficient, the same Eq. (93) that was obtained from the Gibbs distribution, while the second one allows us to calculate the 3rd virial coefficient $C(T)$. (Let me leave the calculation of J_3 and $C(T)$, for the hardball model, for the reader's exercise.) Evidently, a more accurate expansion of Eqs. (110), (112), and (114) may be used to calculate an arbitrary virial coefficient, though starting from the 5th coefficient, such calculations may be completed only numerically even in the simplest hardball model.

3.6. Exercise problems

3.1. Use the Maxwell distribution for an alternative (statistical) calculation of the mechanical work performed (per cycle) by the Maxwell-Demon heat engine discussed in Sec. 2.3.

Hint: You may assume the simplest geometry of the engine – see Fig. 2.4.

3.2.* Use the Maxwell distribution to find the damping coefficient $\eta_p \equiv -\partial P/\partial u$, where P is pressure exerted by an ideal classical gas on a piston moving with very low velocity u , in the simplest geometry shown in Fig. on the right, assuming that collisions of gas particles with the piston are elastic.



3.3.* An ideal gas of $N \gg 1$ classical particles of mass m is confined in a container of volume V . At some moment, a very small hole, of area $A \ll V^{2/3}$, l^2 (where l is the mean free path of the particles) is open in its wall, allowing the particles to escape into the surrounding vacuum. Find the r.m.s. velocity of the escaped particles, assuming that the gas stays in a virtual thermal equilibrium at temperature T .

3.4.* For the system analyzed in the previous problem, calculate the law of reduction of the number of particles in time after opening the hole.

3.5. Derive the equation of state of the ideal classical gas from the grand canonical distribution.

3.6.* A round cylinder of radius R and length L , containing an ideal classical gas of $N \gg 1$ particles of mass m , is rotated about its symmetry axis with angular velocity ω . Assuming that the gas rotates with the cylinder, and is in the thermodynamic equilibrium at temperature T ,

- (i) calculate the gas pressure distribution along its radius, and analyze its temperature dependence,
- (ii) neglecting the internal degrees of freedom of the particles, calculate the total energy of the gas and its heat capacity in the high- and low-temperature limits, and
- (iii) formulate the conditions of validity of your result in terms of strong inequalities between the following length scales: the quantum correlation length $r_c \equiv \hbar/(mT)^{1/2}$, the effective particle size r_0 , the average distance $r_A \equiv (\pi R^2 L/N)^{1/3}$ between the particles, and cylinder's radius R .

Hint: One of considerations in (iii) should be the role of particle's mean free path.

3.7. Prove that Eq. (22), derived for the change of entropy at mixing of two ideal classical gases of completely distinguishable particles (that had equal densities N/V and temperatures T before mixing) is also valid if particles in each of the initial volumes are identical to each other, but different from those in the counterpart sub-volume. Assume that masses of all the particles are equal.

3.8. N classical, non-interacting, indistinguishable particles of mass m are confined in a parabolic, spherically-symmetric 3D potential well $U(\mathbf{r}) = \kappa r^2/2$. Use two different approaches to calculate all major thermodynamic characteristics of the system, in thermal equilibrium at temperature T , including its heat capacity. What of the results should be changed if the particles are distinguishable, and how?

Hint: Suggest a reasonable replacement of the notions of volume and pressure for this system.

3.9.* Calculate the basic thermodynamic characteristics, including all relevant thermodynamic potentials, specific heat, and the surface tension $\sigma \equiv (\partial F/\partial A)_{T,N}$ (where A is the system area), for an ideal 2D electron gas with given areal density $n = N/A$:

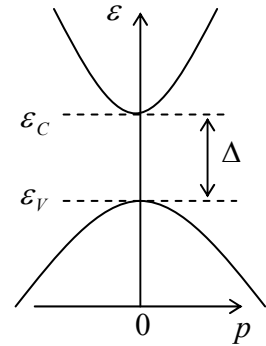
- (i) at $T = 0$, and
- (ii) at low but nonvanishing temperatures (to the first substantial order in $T/\varepsilon_F \ll 1$),

neglecting the Coulomb interaction effects.

3.10. How does the Fermi statistics of an ideal gas affect the barometric formula (28)?

3.11.* Calculate the free carrier density in a semiconductor with bandgap $\Delta \gg T$, assuming isotropic, parabolic dispersion laws of excitations in its conduction and valence bands.

Hint: In semiconductor physics, the names of *conduction* and *valence* bands are used for two adjacent allowed energy bands⁴⁶ that at $T = 0$, all states of the valence band are fully occupied by electrons, while the conduction band is completely empty – see Fig. on the right. Within the simple model mentioned in the assignment (which gives a good approximation for semiconductors of the A_3B_5 group, e.g., GaAs) the energy of an electron-like excitation, with its energy in the conduction band, follows the isotropic, parabolic law (3.3), but with the origin at the band edge ε_C , and an effective mass m_C usually smaller than the free electron mass m_e . Similarly, the parabolic dispersion law of a single “no-electron” excitation (called the *hole*) in the valence band is offset to the edge of that band, ε_V , and corresponds to a negative effective mass ($-m_V$) – see Fig. on the right:



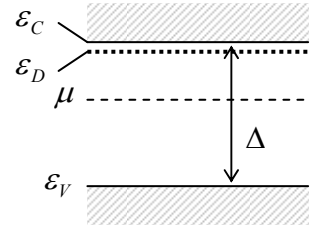
$$\varepsilon = \begin{cases} \varepsilon_C + p^2 / 2m_C, & \text{for } \varepsilon \geq \varepsilon_C, \\ \varepsilon_V - p^2 / 2m_V, & \text{for } \varepsilon \leq \varepsilon_V, \end{cases} \quad \text{where } \varepsilon_C - \varepsilon_V \equiv \Delta.$$

The excitations of both types follow the Fermi-Dirac statistics, and (within this simple model) do not interact directly.

3.12.* Using the same energy band model as in the previous problem, calculate the chemical potential and the equilibrium density of electrons and holes in an n -doped semiconductor, with n_D dopants per unit volume.

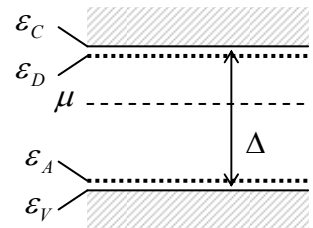
⁴⁶ A discussion of the energy band theory may be found, e.g., in QM Sec. 2.7 and 3.4. Though the reader is highly encouraged to review the discussions of this (very important) topic, such a review is not required for solving this particular problem.

Hint: n -doping means placing, into a semiconductor crystal, a relatively small density n_D of different atoms, called *dopants* or *donors*, which may be easily single-ionized - in the case of donors, giving an additional electron to the semiconductor crystal, with the donor atom becoming a positive ion. As a result, the n -doping may be represented as a set of additional electrons with the ground state energy on an additional discrete level ε_D slightly below the conduction band edge ε_C – see Fig. on the right.



3.13.* Generalize the solution of the previous problem to the case when the n -doping with dopant density n_D is complemented with the simultaneous p -doping by *acceptor* atoms, whose energy of accepting an additional electron (and hence the negative ionization) is much less than the bandgap.

Hint: Similarly to the n -doping, the effect of p -doping may be described as an addition of a discrete electron energy level ε_A , slightly above the valence band edge ε_V – see Fig. on the right.



3.14. Calculate the paramagnetic response (the *Pauli paramagnetism*) of a degenerate ideal gas of spin- $\frac{1}{2}$ particles to a weak external magnetic field, due to partial spin alignment with the field.

3.15.* Explore the *Thomas-Fermi model*⁴⁷ of a heavy atom, with nuclear charge $Q = Ze \gg e$, in which the electrons are treated as a degenerate Fermi gas, interacting with each other only via their contribution to the common electrostatic potential $\phi(\mathbf{r})$. In particular, derive the ordinary differential equation obeyed by the radial distribution of the potential, and use it to estimate the effective radius of the atom.

3.16.* Use the Thomas-Fermi model, explored in the previous problem, to calculate the total binding energy of a heavy atom. Compare the result with that for the simpler model, in which the electron-electron interaction is completely ignored.

3.17. Derive the general expressions for the calculation of energy E and chemical potential μ of a Fermi gas of N non-interacting, indistinguishable, ultrarelativistic particles confined in volume V .⁴⁸ Calculate E , and also gas pressure P explicitly in the degenerate gas limit $T \rightarrow 0$. In particular, is Eq. (3.48) of the lecture notes, $PV = (2/3)E$, valid in this case?

3.18. Calculate the pressure of an ideal gas of ultra-relativistic, indistinguishable quantum particles, for an arbitrary temperature, as a function of the total energy E of the gas, and its volume V . Compare the result with the corresponding relations for the electromagnetic blackbody radiation and an ideal gas of nonrelativistic particles.

3.19.* Calculate the speed of sound in an ideal gas of ultra-relativistic fermions of density n at negligible temperature.

⁴⁷ It was suggested in 1927, independently, by L. Thomas and E. Fermi.

⁴⁸ This is, for example, an approximate model for electrons in white dwarf stars, whose Coulomb interaction is mostly compensated by the charge of nuclei of fully ionized helium atoms.

3.20. Calculate the effective latent heat $\Lambda \equiv -N(\partial Q/\partial N_0)_{N,V}$, of the Bose-Einstein condensate evaporation, as a function of temperature T . Here Q is the heat absorbed by the (condensate + gas) system as a whole, while N_0 is the number of particles in the condensate alone.

3.21. * For an ideal Bose gas, calculate the law of the chemical potential disappearance at $T \rightarrow T_c$, and use the result to prove that the gas' specific heat C_V is a continuous function of temperature at the critical point $T = T_c$.

3.22. In Chapter 1 of the lecture notes, several thermodynamic equations involving entropy have been discussed, including the first of Eqs. (1.39):

$$S = -(\partial G / \partial T)_p.$$

If we combine this expression with the fundamental relation (1.56), $G = \mu N$, it looks like that for the Bose-Einstein condensate, whose chemical potential μ vanishes at temperatures below the critical value T_c , the entropy should vanish as well. On the other hand, dividing both parts of Eq. (1.19) by dT , and assuming that at this temperature change the volume is kept constant, we get

$$C_V = T(\partial S / \partial T)_V.$$

If C_V is known as a function of temperature, the last equation may be integrated to calculate S :

$$S = \int_{V=\text{const}} \frac{C_V(T)}{T} dT + \text{const.}$$

For the Bose-Einstein condensate, we have calculated the specific heat to be proportional to $T^{3/2}$, so that the integration gives nonvanishing entropy $S \propto T^{3/2}$. Explain this paradox.

3.23. The standard approach to the Bose-Einstein condensation, outlined in Sec. 4, may seem to ignore the energy quantization of particles confined in volume V . Use the particular case of a cubic confining volume $V = a \times a \times a$ with rigid walls to analyze whether the main conclusions of the standard theory, in particular Eq. (71) for the critical temperature, are affected by such quantization.

3.24. * An ideal 3D Bose gas of $N \gg 1$ non-interacting particles is confined at the bottom of a soft, spherically-symmetric potential well, whose potential may be approximated as $U(\mathbf{r}) = m\omega^2 r^2/2$. Develop the theory of the Bose-Einstein condensation in this system; in particular, prove Eq. (3.74b) of the lecture notes, and calculate the critical temperature T_c^* . Looking at the solution, what is the most straightforward way to detect the condensation?

3.25. Calculate the chemical potential of an ideal 2D gas of spin-0 Bose particles as a function of its areal density n (the number of particles per unit area), and find out whether such a gas can condense at low temperatures.

3.26. * Use Eqs. (115) and (120) to calculate the third virial coefficient $C(T)$ for the hardball model of particle interactions.

Chapter 4. Phase Transitions

This chapter is a brief discussion of coexistence between different states (“phases”) of collections of the same particles, and the laws of transitions between these phases. Due to the complexity of these phenomena, which involve interaction of the particles, quantitative results have been obtained only for a few very simple models, typically giving only a very approximate description of real systems.

4.1. First-order phase transitions

From everyday experience, say with ice, water, and water vapor, we know that one chemical substance (i.e. a set of many similar particles) may exist in several stable states - *phases*. A typical substance may have:

- (i) a dense *solid phase*, in which interatomic forces keep all atoms in fixed relative positions, with just small thermal fluctuations about them;
- (ii) a *liquid phase*, of comparable density, in which the relative distances between atoms or molecules are almost constant, but the particles are free to move about each other, and
- (iii) the *gas phase*, typically of a much lower density, in which the molecules are virtually free to move all around the containing volume.¹

Experience also tells us that at certain conditions, two phases may be in thermal and chemical equilibrium – say, ice floating on water, with temperature at the freezing point. Actually, in Sec. 3.4 we already discussed a qualitative theory of one such equilibrium, the Bose-Einstein condensate coexistence with the uncondensed “vapor” of similar particles. However, this is a rather rare case when the phase coexistence is due to the quantum nature of particles (bosons) that may not interact directly. Much more frequently, the formation of different phases, and transitions between them, is an essentially classical effect due to particle interactions.

Phase transitions are sometimes classified by their *order*.² I will start my discussion with the *first-order phase transitions* that feature non-vanishing *latent heat* Λ - the amount of heat that is necessary to give to one phase in order to turn it into another phase, even if temperature and pressure are kept constant.³ Let us discuss the most simple and popular phenomenological model of the first-order phase transition, suggested in 1873 by J. van der Waals.

In the last chapter, we have derived Eq. (3.99) for the classical gas of weakly interacting particles, which takes into account (albeit approximately) both interaction components necessary for a

¹ The plasma phase, in which atoms are partly or completely ionized, is frequently mentioned in the same breath as the three phases listed above, but one has to remember that in contrast to them, a typical electroneutral plasma consists of particles of two different sorts – ions and electrons.

² Such classification schemes, started by P. Ehrenfest, have been repeatedly modified, and only the “first-order phase transition” is still a generally accepted term.

³ For example, for water the latent heat of vaporization at ambient pressure is as high as $\sim 2.2 \times 10^6$ J/kg, i.e. ~ 0.4 eV per molecule, making this liquid indispensable for many practical purposes - including fire fighting. (The latent heat of water’s ice melting is an order of magnitude lower.)

realistic discussion of gas condensation – the long-range attraction of the particles and their short-range repulsion. Let us rewrite that result as follows:

$$P + a \frac{N^2}{V^2} = \frac{NT}{V} \left(1 + \frac{Nb}{V} \right). \quad (4.1)$$

As we saw in Sec. 3.5, the physical meaning of constant b is the effective volume of space taken by a particle pair collision. Equation (1) is quantitatively valid only if the second term in the parentheses is small, $Nb \ll V$, i.e. if the total volume excluded from particles' free motion because of their collisions is much smaller than the whole volume V of the system. In order to describe the condensed phase (which I will call “liquid”),⁴ we need to generalize this relation to the case $Nb \sim V$. Since the effective volume left for particles' motion is $V - Nb$, it is very natural to make the following replacement: $V \rightarrow V - Nb$, in the ideal gas' equation of state. If we still keep the term aN^2/V^2 , which describes the long-range attraction of particles, we get the *van der Waals equation*

$$P + a \frac{N^2}{V^2} = \frac{NT}{V - Nb}. \quad (4.2)$$

Van der
Waals
equation

The advantage of this simple model is that in the rare gas limit, $Nb \ll V$, it reduces back to Eq. (1). (To check this, it is sufficient to Taylor-expand the right-hand part of Eq. (2) in small parameter $Nb/V \ll 1$, and retain only two leading terms corresponding to two first virial coefficients.) Let us explore properties of this model.

It is frequently convenient to discuss any equation of state in terms of its isotherms, i.e. $P(V)$ curves plotted at constant T . As Eq. (2) shows, in the van der Waals model such a plot depends on 4 parameters (a , b , N , and T .) However, for its analysis it is convenient to introduce dimensionless variables: pressure $p \equiv P/P_c$, volume $v \equiv V/V_c$, and temperature $t \equiv T/T_c$, normalized to their so-called *critical values*,

$$P_c \equiv \frac{1}{27} \frac{a}{b^2}, \quad V_c \equiv 3Nb, \quad T_c \equiv \frac{8}{27} \frac{a}{b}. \quad (4.3)$$

In these notations, Eq. (2) acquires the following form,

$$\left(p + \frac{3}{v^2} \right) = \frac{8t}{(3v-1)}, \quad (4.4)$$

so that the normalized isotherms $p(v)$ depend on only one parameter, the normalized temperature t – see Fig. 1. The most important property of these plots is that the isotherms have qualitatively different shapes in two temperature regions.⁵ At $t > 1$, i.e. $T > T_c$, pressure increases monotonically at gas compression (just like in an ideal gas, to which this system tends at $T \gg T_c$), i.e. $(\partial P/\partial V)_T < 0$ at all points of the isotherm. However, below the critical temperature T_c , all isotherms feature segments with $(\partial P/\partial V)_T > 0$. It is easy to understand that, as least in a constant pressure experiment (see, for example,

⁴ Due to the phenomenological character of the van der Waals model, one cannot say whether the condensed phase it predicts corresponds to a liquid or a solid. However, in most real substances at ambient conditions, gas coexists with liquid, hence the name I will use.

⁵ The special choice of numerical coefficients in Eq. (3) is motivated by making the border between two regions to take place exactly at $t = 1$, i.e. at temperature T_c , with the critical point coordinates equal to P_c and V_c .

Fig. 1.5),⁶ these segments describe a mechanically unstable equilibrium. Indeed, if due to a random fluctuation, the volume deviated upward from the equilibrium value, the pressure would also increase, forcing the environment (say, the heavy piston in Fig. 1.5) to allow a further expansion of the system, leading to even higher pressure, etc. A similar deviation of volume downward would lead to a similar avalanche-like decrease of the volume. Such avalanche instability would develop further and further until the system has reached one of the stable branches with a negative slope $(\partial P/\partial V)_T$. In the range where the single-phase equilibrium state is unstable, the system as a whole may be stable only if it consists of the two phases (one with a smaller, and another with a higher density $n = N/V$) that are described by the two stable branches.

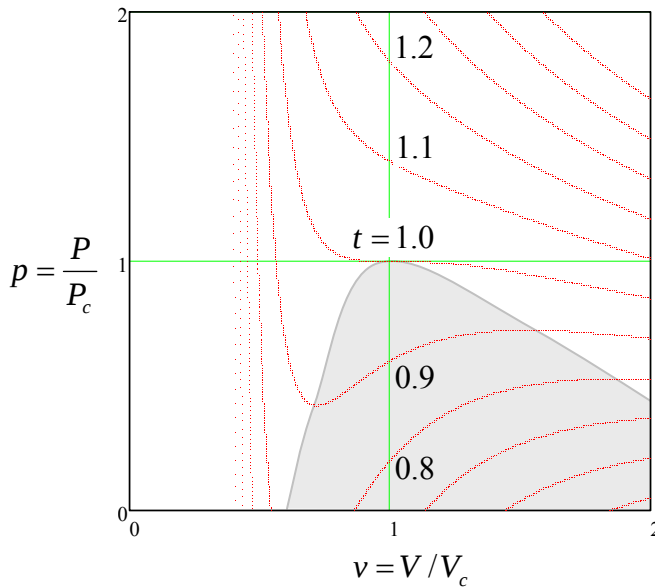


Fig. 4.1. The van der Waals equation plotted on the $[p, v]$ plane for several values of reduced temperature $t \equiv T/T_c$. Shading shows the single-phase instability range in which $(\partial P/\partial V)_T > 0$. (The reader is invited to contemplate the physical sense and possibility of experimental observation of the negative values of pressure, predicted by the model.)

In order to understand the basic properties of this two-phase system, let us recall the general conditions of equilibrium of two thermodynamic systems, which have been discussed in Chapter 1:

$$T_1 = T_2 \text{ (thermal equilibrium),} \quad (4.5)$$

$$\mu_1 = \mu_2 \text{ ("chemical" equilibrium),} \quad (4.6)$$

Phase
equilibrium
conditions

the latter condition meaning that the average energy of a single ("probe") particle in both systems is the same. To those, we should add the evident condition of mechanical equilibrium,

$$P_1 = P_2 \text{ (mechanical equilibrium),} \quad (4.7)$$

that immediately follows from the balance of normal forces exerted on an inter-phase boundary.

If we discuss isotherms, Eq. (5) is fulfilled automatically, while Eq. (7) means that the effective isotherm $P(V)$ describing a two-phase system should be a horizontal line (Fig. 2):⁷

⁶ Actually, this assumption is not crucial for our analysis of mechanical stability, because if a fluctuation takes place in a small part of the total volume V , its other parts play the role of pressure-fixing environment.

⁷ Frequently, especially for water gas diluted in air (*vapor*), $P_0(T)$ is called the *saturated vapor pressure*, while the temperature at which $P_0(T)$ equals to the ambient pressure, is called the *dew point*, and its frequently used for an implicit characterization of the concentration $n = N/V$ of water vapor in air.

$$P = P_0(T). \quad (4.8)$$

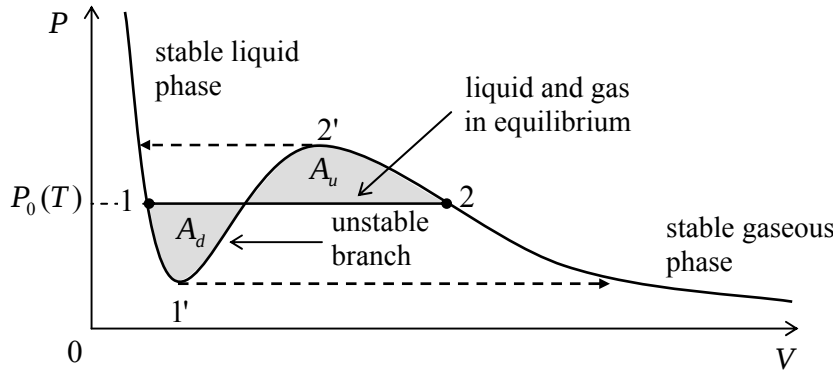


Fig. 4.2. Phase equilibrium at $T < T_c$ (schematically).

Along this line, internal properties of each phase do not change; only the particle distribution is: it evolves gradually from all particles being in the liquid phase at point 1 to all particles being in the gas phase at point 2.⁸ In particular, according to Eq. (6), the chemical potentials μ of the phases should be equal at each point of the horizontal line (8). This fact enables us to find the line's position: it has to connect points 1 and 2 in which the chemical potentials of the phases are equal to each other.

Let us recast this condition as

$$\int_1^2 d\mu = 0, \quad \text{i.e.} \quad \int_1^2 dG = 0, \quad (4.9)$$

where the integral may be taken along the single-phase isotherm. (For this mathematical calculation, the mechanical instability of some states on this curve is not important.) Along that curve, $N = \text{const}$ and $T = \text{const}$, so that according to Eq. (1.53c), $dG = -SdT + VdP + \mu dN$, for a slow (reversible) change, $dG = VdP$. Hence Eq. (9) yields

$$\int_1^2 VdP = 0. \quad (4.10)$$

From Fig. 2, it is easy to see that geometrically this equality means that the shaded areas A_d and A_u should be equal, and hence Eq. (10) may be rewritten in the form of the so-called *Maxwell's rule*

$$\boxed{\int_1^2 [P - P_0(T)] dV = 0.} \quad (4.11) \quad \text{Maxwell's rule}$$

⁸ An important question is: why does the phase-equilibrium line $P = P_0(T)$ stretch all the way from point 1 to point 2 (Fig. 2)? Indeed, branches 1-1' and 2-2' of the single-phase isotherm have negative derivative $(\partial P/\partial V)_T$ and hence are mechanically stable to small perturbations. The answer is that these branches are actually *metastable*, i.e. have larger Gibbs energy per particle (i.e. μ) than the counterpart phase and are hence unstable to *larger* perturbations - such as foreign microparticles (say, dust), confining wall protrusions, etc. In very controlled conditions, these single-phase "superheated" or "supercooled" states can survive virtually all the way to zero-derivative points 1' and 2', leading to sudden jumps of the system into the counterpart phase. (For fixed-pressure conditions, such jumps are shown by dashed lines in Fig. 2.) However, at more realistic conditions, perturbations result in the two-phase coexistence extending all the way between (or very close to) points 1 and 2.

This relation is more convenient for calculations than Eq. (10) if the equation of state may be explicitly solved for P – as it is the case for the van der Waals equation (2). Such calculation (left for reader's exercise) shows that for that model, the temperature dependence of the saturated gas pressure at low T is exponential,

$$P_0(T) = 27P_c \exp\left\{-\frac{U_0}{T}\right\}, \quad \text{with } U_0 \equiv \frac{a}{b} = \frac{27}{8}T_c, \quad \text{for } T \ll T_c, \quad (4.12)$$

corresponding very well to the physical picture of the rate of particle activation from the potential well of depth U_0 .⁹

The signature parameter of the first-order phase transition, the latent heat of evaporation

Latent
heat:
definition

$$\Lambda \equiv \int_1^2 dQ, \quad (4.13)$$

may be found by a similar integration along the single-phase isotherm. Indeed, using Eq. (1.19), $dQ = TdS$, we get

$$\Lambda \equiv \int_1^2 TdS = T(S_2 - S_1). \quad (4.14)$$

Instead of calculating entropy from the equation of state (as was done for the ideal gas in Sec. 1.4), it is easier to express the right-hand side of Eq. (14) directly via that equation. For that, let us take the full derivative of Eq. (6) over temperature, considering each value of $G = N\mu$ as a function of P and T , and taking into account that according to Eq. (7), $P_1 = P_2 = P_0(T)$:

$$\left(\frac{\partial G_1}{\partial T}\right)_P + \left(\frac{\partial G_1}{\partial P}\right)_T \frac{dP_0}{dT} = \left(\frac{\partial G_2}{\partial T}\right)_P + \left(\frac{\partial G_2}{\partial P}\right)_T \frac{dP_0}{dT}. \quad (4.15)$$

According to the first of Eqs. (1.39), the partial derivative $(\partial G/\partial T)_P$ is just minus entropy, while according to the second of those equations, $(\partial G/\partial P)_T$ is the volume. Thus Eq. (15) becomes

$$-S_1 + V_1 \frac{dP_0}{dT} = -S_2 + V_2 \frac{dP_0}{dT}. \quad (4.16)$$

Solving this equation for $(S_2 - S_1)$, and plugging the result into Eq. (14), we get the *Clapeyron-Clausius formula*

Clapeyron-
Clausius
formula

$$\Lambda = T(V_2 - V_1) \frac{dP_0}{dT}. \quad (4.17)$$

For the van der Waals model, this formula may be readily used for the analytical calculation of Λ may in two limits: $T \ll T_c$ and $(T_c - T) \ll T_c$ – the exercise left for the reader. In the latter limit, $\Lambda \propto (T_c - T)^{1/2}$, naturally vanishing at the critical temperature.

Finally, some important properties of the van der Waals' model may be revealed more easily by looking at the set of its isochores $P = P(T)$ for $V = \text{const}$, rather than at the isotherms. Indeed, as Eq. (2) shows, all single-phase isochores are straight lines. However, if we interrupt these lines at the points

⁹ It is fascinating how well is this Arrhenius exponent hidden in the polynomial van der Waals equation (2)!

when the single phase becomes metastable, and complement them with the (very nonlinear!) dependence $P_0(T)$, we get the pattern (called the *phase diagram*) shown schematically in Fig. 3a.

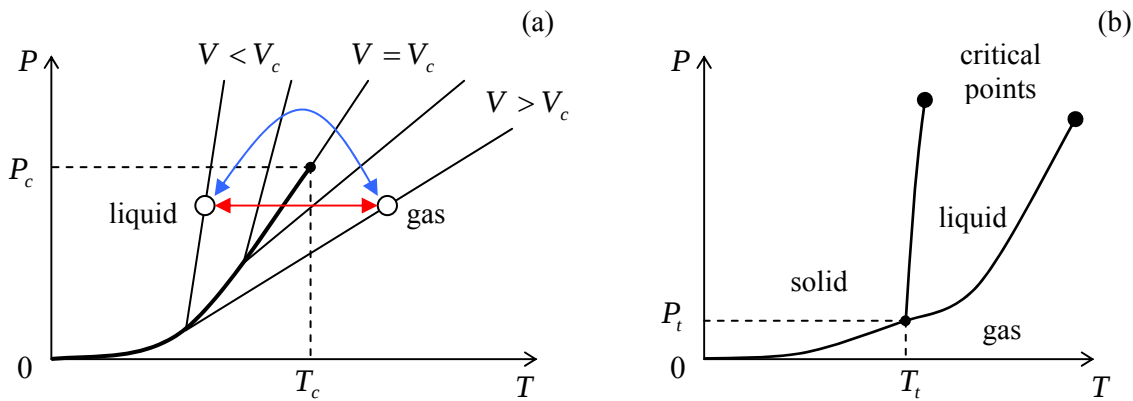


Fig. 4.3. (a) The van der Waals model's isochores, the saturated gas pressure diagram and the critical point, and (b) the phase diagram of a typical 3-phase system (schematically).

At this plot, one more meaning of the critical point $\{P_c, T_c\}$ becomes very clear. At fixed pressure $P < P_c$, the liquid and gaseous phases are clearly separated by the transition line $P_0(T)$, so if we achieve the transition just by changing temperature, and hence volume (shown with the red line in Fig. 3), we will pass through the phase coexistence stage. However, if we perform the same final transition by changing both the pressure and temperature, going around above the critical point (the blue line in Fig. 3), no definite point of transition may be observed: the substance stays in a single phase, and it is a subjective judgment of the observer in which region that phase should be called the liquid, and which region the gas. For water, the critical point corresponds to 647 K (374°C) and $P_c \approx 22.1$ MPa (i.e. ~ 200 bars), so that a lecture demonstration of its critical behavior would require substantial safety precautions. This is why such demonstrations are typically carried out with other fluids such as the diethyl ether,¹⁰ with much lower T_c (194 °C) and P_c (3.6 MPa). Though the ether is colorless and clear in both gas and liquid phases, their separation (due to gravity) is visible (due to a difference in an optical refraction coefficient) at $P < P_c$, but not above P_c .¹¹

Thus, in the van der Waals model, two phases may coexist, though only at certain conditions ($P < P_c$). Now the natural question is whether the coexistence of more than two phases of the same substance is possible. For example, can the water ice, liquid water, and water vapor (steam) be in thermodynamic equilibrium? The answer is essentially given by Eq. (6). From thermodynamics, we know that for a uniform system (with $G = \mu N$), pressure and temperature completely define the chemical potential. Hence, dealing with two phases, we have to satisfy just *one* chemical equilibrium condition (6) for *two* common parameters P and T . Evidently, this leaves us with one extra degree of freedom, so

¹⁰ $(\text{CH}_3\text{-CH}_2)\text{-O-(CH}_2\text{-CH}_3)$, historically the first popular general anesthetic.

¹¹ It is interesting that very close to the critical point the substance suddenly becomes opaque - in the case of ether, whitish. The qualitative explanation of this effect, called the *critical opalescence*, is simple: at this point the difference of Gibbs energies per particle (i.e. chemical potentials) of the two phases becomes so small that the unavoidable thermal fluctuations lead to spontaneous appearance and disappearance of relatively large (a-few- μm -scale) single-phase regions in all the volume. Since the optical refraction coefficients of the phases are slightly different, large concentration of the region boundaries leads to strong light scattering.

that the two-phase equilibrium is possible within a certain range of P at fixed T (or vice versa) – see Fig. 3a. Now, if we want *three* phases to be in equilibrium, we need to satisfy *two* equations for these variables:

$$\mu_1(P, T) = \mu_2(P, T) = \mu_3(P, T). \quad (4.18)$$

Typically, functions $\mu(P, T)$ are monotonic, so that Eqs. (18) have just one solution, the so-called *triple point* $\{P_t, T_t\}$. Of course, the triple point $\{P_t, T_t\}$ of equilibrium between *three* phases should not be confused with the critical points $\{P_c, T_c\}$ of transitions between *two* phase pairs. Fig. 3b shows, very schematically, their relation for a typical three-phase system solid-liquid-gas. For example, water, ice, and water vapor are at equilibrium at a triple point corresponding to 0.612 KPa and (by definition, exactly) 273.16 K.¹² The particular importance of this particular temperature point is that by an international agreement it has been accepted for the Celsius scale definition, as 0.01°C, so that the absolute temperature zero corresponds to exactly -273.15°C. More generally, triple points of pure substances (such as H₂, N₂, O₂, Ar, Hg, and H₂O) are broadly used for thermometer calibration, defining the so-called *international temperature scales* including the currently accepted scale ITS-90.

This result may be readily generalized to multi-component systems consisting of particles of several (say, L) sorts.¹³ If such a system is in a single phase, i.e. macroscopically uniform, its chemical potential may be defined by the natural generalization of Eq. (1.53c):

$$dG = -SdT + VdP + \sum_{l=1}^L \mu^{(l)} dN^{(l)}. \quad (4.19)$$

Typically, a single phase is not a pure substance, but has certain concentrations of other components, so that $\mu^{(l)}$ may depend not only on P and T , but also on *concentrations* $c^{(l)} \equiv N^{(l)}/N$ of particles of each sort. If the total number N of particles is fixed, the number of independent concentrations is $(L - 1)$. For the chemical equilibrium of R phases, all R values of $\mu_r^{(l)}$ ($r = 1, 2, \dots, R$) have to be equal for particles of each sort: $\mu_1^{(l)} = \mu_2^{(l)} = \dots = \mu_R^{(l)}$, with each $\mu_r^{(l)}$ depending on $(L - 1)$ concentrations $c_r^{(l)}$, and also on P and T . This requirement gives $L(R - 1)$ equations for $(L - 1)R$ concentrations $c_r^{(l)}$, plus two common arguments P and T , i.e. for $[(L - 1)R + 2]$ independent variables. This means that the number of phases has to satisfy the limitation

$$L(R - 1) \leq (L - 1)R + 2, \quad \text{i.e. } R \leq L + 2, \quad (4.20)$$

where the equality sign may be reached in just one point in the whole parameter space. This is the *Gibbs phase rule*. As a sanity check, for a single-component system, $L = 1$, the rule yields $R \leq 3$ – exactly the result we have already discussed.

4.2. Continuous phase transitions

As Fig. 2 shows, if we fix pressure P in a system with a first-order phase transition, and start changing its temperature, crossing the transition point, defined by equation $P_0(T) = P$, requires the

¹² Please note that P_t for water is several orders of magnitude lower than P_c of the water-vapor transition, so that Fig. 3b is indeed very much not to scale!

¹³ Perhaps the most practically important example is the air/water system. For its detailed discussion, based on Eq. (19), the reader may be referred, e.g., to Sec. 3.9 in F. Schwabl, *Statistical Mechanics*, Springer (2000). Other important applications include metallic *alloys* – solid solutions of metal elements.

insertion (or extraction) the finite latent heat Λ . Relations (14) and (17) show that the latent heat is directly related to the finite difference between entropies and volumes of the two phases (at the same pressure). As we know from Chapter 1, both S and V may be presented as first derivatives of appropriate thermodynamic potentials. This is why such transitions, involving a jump of potentials' *first* derivatives, are called *first-order* phase transitions.

On the other hand, there are phase transitions that have zero latent heat ($\Lambda = 0$) and no first derivative jumps at the transition temperature T_c , so that the temperature point is clearly marked, for example, by a jump of a *second* derivative of a thermodynamic potential - for example, the derivative $\partial C/\partial T$ which, according to Eq. (1.24), equals to $\partial^2 E/\partial T^2$. In the initial classification by P. Ehrenfest, this was an example of a *second-order* phase transition. However, most features of such phase transitions are also pertinent to some systems in which the second derivatives of potentials are continuous as well. Due to this reason, I will use a more recent terminology (suggested by M. Fisher), in which all phase transitions with $\Lambda = 0$ are called *continuous*.

Most continuous phase transitions result from particle interactions. Here are some examples:

(i) At temperatures above $\sim 120^\circ\text{C}$, the crystal lattice of barium titanate (BaTiO_3) is cubic, with a Ba ion in the center of each Ti-cornered cube (or vice versa) – see Fig. 4a. However, as temperature is being lowered below that critical value, the sublattice of Ba ions starts moving along one of 6 sides of the TiO_3 sublattice, leading to a small deformation of both lattices - which become tetragonal. This is a typical example of a *structural transition*, in this particular case combined with a *ferroelectric transition*, because (due to the positive electric charge of Ba ions) below the critical temperature the BaTiO_3 crystal acquires a spontaneous electric polarization.

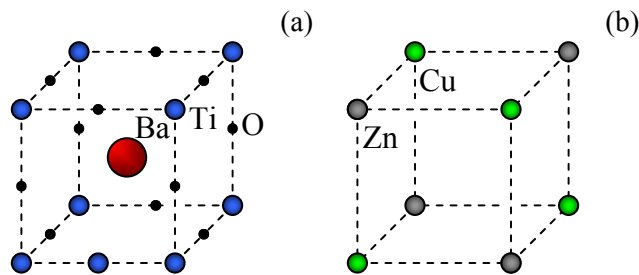


Fig. 4.4. Cubic lattices of (a) BaTiO_3 and (b) CuZn .

(ii) A different kind of phase transition happens, for example, in $\text{Cu}_x\text{Zn}_{1-x}$ alloys (*brasses*). Their crystal lattice is always cubic, but above certain critical temperature T_c (which depends on x) any of its nodes is occupied by either a copper or a zinc atom, at random. At $T < T_c$, a trend towards atom alternation arises, and at low temperatures, the atoms are fully ordered, as shown in Fig. 4b for the stoichiometric case $x = 0.5$. This is a good example of an *order-disorder* transition.

(iii) At *ferromagnetic* transitions (happening, e.g., in Fe at 1,388 K) and *antiferromagnetic* transitions (e.g., in MnO at 116 K), lowering of temperature below the critical value¹⁴ does not change atom positions substantially, but results in a partial ordering of atomic spins, eventually leading to their full ordering (Fig. 5).

¹⁴ For ferromagnets, this point is usually referred to as the *Curie temperature*, and for antiferromagnets, as the *Néel temperature*.

(iv) Finally, the *Bose-Einstein condensation* of atoms in liquid helium and electrons in superconducting metals and metal oxides may be also considered as continuous phase transitions. At the first glance, this contradicts to the nonvanishing latent heat given by the BEC theory outlined in Sec. 3.4. However, that theory shows that $\Lambda \rightarrow 0$ at $T \rightarrow 0$ and hence $P(T) \rightarrow 0$ – see Eq. (3.79). Hence, at zero pressure the Bose-Einstein condensation of an ideal gas could be considered a continuous phase transition. For a gas, this is just not a very interesting limit, because of the vanishing gas density. On the contrary, the Bose-Einstein condensation of strongly interacting particles in liquids or solids is not affected by pressure – at least on the ambient pressure scale, and taking $P = 0$ is quite a legitimate assumption.¹⁵

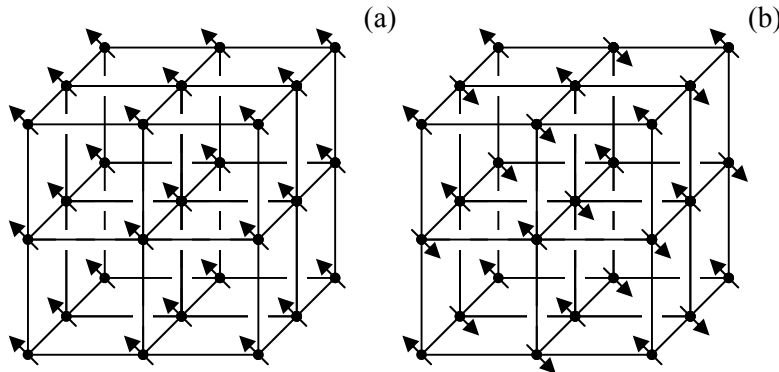


Fig. 4.5. Classical images of completely ordered phases: (a) a ferromagnet, and (b) an antiferromagnet.

Besides these standard examples, some other threshold phenomena, such as formation of a coherent optical field in a laser, and even the self-excitation of oscillators with negative damping (see, e.g., CM Sec. 4.4), may be treated, at certain conditions, as continuous phase transitions.¹⁶

The general feature of all these transitions is the gradual formation, at $T < T_c$, of certain *ordering*, which may be characterized by some *order parameter* $\eta \neq 0$. The simplest example of such order parameter is the magnetization at the ferromagnetic transitions, and this is why the continuous phase transitions are usually discussed on certain models of ferromagnetism. (I will follow this tradition, while mentioning in passing other important cases that require a substantial modification of theory.) Most of such models are defined on an infinite 3D cubic lattice (see, e.g., Fig. 5), with evident generalizations to lower dimensions. For example, the *Heisenberg model* of a ferromagnet is defined by the following Hamiltonian:

$$\hat{H} = -J \sum_{\langle j, j' \rangle} \hat{\mathbf{g}}_j \cdot \hat{\mathbf{g}}_{j'} - \sum_j \mathbf{h} \cdot \hat{\mathbf{g}}_j, \quad \text{with } \mathbf{h} \equiv \mu_B \mathcal{B}, \quad (4.21)$$

Heisenberg
model

¹⁵ As follows from the discussion of Eqs. (1.1)–(1.3), for ferroelectric transitions between phases with different electric polarization, the role of pressure is played by the external electric field $\mathcal{E}$, while for the ferromagnetic transitions between phases with different magnetization, by the external magnetic field $\mathcal{H}$. As we will see very soon, such fields give such a phase transition a nonvanishing latent heat, making it the first order transition.

¹⁶ Unfortunately, I will have no time for these interesting (and practically important) generalizations, and have to refer the interested reader to the famous monograph by R. Stratonovich, *Topics in the Theory of Random Noise*, in 2 vols., Gordon and Breach, 1963 and 1967, and/or the influential review by H. Haken, *Ferstkörperprobleme* **10**, 351 (1970).

where $\hat{\sigma}_j$ is the Pauli matrix operator¹⁷ acting on j -th spin, $\mathbf{n}_{\mathcal{B}}$ is the direction of magnetic field $\mathcal{B}$, and constant μ_B is the *Bohr magneton*

$$\mu_B = \frac{e\hbar}{2m_e} \approx 0.927 \times 10^{-23} \text{ J/T}, \quad (4.22)$$

with $(-e)$ and m_e being electron's charge and mass. The figure brackets $\{j, j'\}$ in Eq. (21) denote the summation over the pairs of adjacent sites, so that the magnitude of constant J may be interpreted as the maximum coupling energy per “bond” between two adjacent particles. At $J > 0$, the coupling tries to keep spins aligned (thus minimizing the coupling energy), i.e. to implement the ferromagnetic ordering.¹⁸ The second term in Eq. (21) describes the effect of external magnetic field $\mathcal{B}$, which tries to turn all spins, with their magnetic moments, along its direction.

However, even the Heisenberg model, while being approximate, is still too complex for analysis. This is why most theoretical results have been obtained for its classical twin, the *Ising model*:¹⁹

$$E_m = -J \sum_{\{j, j'\}} s_j s_{j'} - h \sum_j s_j. \quad (4.23) \quad \text{Ising model}$$

Here E_m are eigenvalues of energy in the magnetic field, constant h mimics an external magnetic field, and s_j are classical scalar variables that may take only two values, $s_j = \pm 1$. (Despite its classical character, variable s_j modeling the real spin of an electron, is usually called “spin” for brevity, and I will follow this tradition.) Index m numbers all possible combinations of variables s_j – there are 2^N of them in a system of N Ising “spins”. Somewhat shockingly, even for this toy model, no analytical 3D solutions have been found, and the solution of its 2D version by L. Onsager in 1944 (see Sec. 5 below) is still considered one of the top intellectual achievements of the statistical physics. Still, Eq. (23) is very useful for the introduction of basic notions of continuous phase transitions, and methods of their analysis, and I will focus my brief discussion on this model.²⁰

Evidently, if $T = 0$ and $h = 0$, the lowest value of internal energy,

$$E_{\min} = -JNd, \quad (4.24)$$

where d is the lattice dimensionality, is achieved in the “ferromagnetic” phase in which all spins s_j are equal to either $+1$ or -1 simultaneously, so that the lattice average $\langle s_j \rangle = \pm 1$. On the other hand, at $J = 0$ and $h = 0$, the spins are independent, and in the absence of external field their signs are completely random, with the 50% probability to have either of values ± 1 , so that $\langle s_j \rangle = 0$. Hence in the case of arbitrary parameters we may use the average

¹⁷ See, e.g., QM Sec. 4.4.

¹⁸ At $J < 0$, the first term of Eq. (21) gives a reasonable model of an antiferromagnet, but in this case the external magnetic field effects are more subtle, so I will not have time to discuss it.

¹⁹ Named after E. Ising who explored the 1D version of the model in detail in 1925, though a similar model was discussed earlier (in 1920) by W. Lenz.

²⁰ For a more detailed discussion of phase transition theory (including other popular models of the ferromagnetic phase transition, e.g., the Potts model), see, e.g., either H. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Oxford U. Press, 1971; or A. Patashinskii and V. Pokrovskii, *Fluctuation Theory of Phase Transitions*, Pergamon, 1979; or B. McCoy, *Advanced Statistical Mechanics*, Oxford U. Press, 2010. For a much more concise text, I can recommend J. Yeomans, *Statistical Mechanics of Phase Transitions*, Clarendon, 1992.

$$\eta \equiv \langle s_j \rangle \quad (4.25)$$

as a good measure of spin ordering, i.e. as the order parameter. Since in a real ferromagnet, each spin carries a magnetic moment, the order parameter η corresponds to the substance *magnetization*, at $\eta h > 0$, directed along the applied magnetic field.²¹

Due to the difficulty of calculating the order parameter for arbitrary temperatures, most theoretical discussions of continuous phased transitions are focused on its temperature dependence just below T_c . Both experiment and theory show that (in the absence of external field) this dependence is close to a certain power,

$$\eta \propto \tau^\beta, \quad \text{for } \tau > 0, \quad (4.26)$$

of the small deviation from the critical temperature, which is conveniently normalized as

$$\tau \equiv \frac{T_c - T}{T_c}. \quad (4.27)$$

Remarkably, most other key variables follow a similar temperature behavior, with the same *critical exponent* for both signs of τ . In particular, the heat capacity at fixed magnetic field behaves as²²

$$C_h \propto \frac{1}{|\tau|^\alpha}. \quad (4.28)$$

Similarly, the (normalized) low-field *susceptibility*²³

$$\chi \equiv \left. \frac{\partial \eta}{\partial h} \right|_{h=0} \propto \frac{1}{|\tau|^\gamma}. \quad (4.29)$$

Two more important critical exponents, ζ and ν , describe temperature behavior of the *correlation function* $\langle s_j s_{j'} \rangle$ whose dependence on distance $r_{jj'}$ between two spins may be well fitted by the following law,

$$\langle s_j s_{j'} \rangle \propto \frac{1}{r_{jj'}^{d-2+\zeta}} \exp \left\{ -\frac{r_{jj'}}{r_c} \right\}, \quad (4.30)$$

with the *correlation radius*

$$r_c \propto \frac{1}{|\tau|^\nu}. \quad (4.31)$$

Finally, three more critical exponents, usually denoted ε , δ , and μ , describe the external field dependences of, respectively, c , η and r_c at $\tau = 0$. For example, δ is defined as

²¹ See, e.g., EM Secs. 5.4-5.5.

²² The form of all temperature functions is selected so that all critical exponents are non-negative.

²³ This variable models the real physical magnetic susceptibility χ_m of magnetic materials – see, e.g., EM Eq. (5.111).

$$\eta \propto h^{1/\delta} . \quad (4.32)$$

(Other field exponents are used less frequently, and for their discussion I have to refer the interested reader to the special literature listed above.)

The second column of Table 1 shows experimental values of the critical exponents for various 3D physical systems featuring continuous phase transitions. One can see that their values vary from system to system, leaving no hope for a universal theory that would describe them all. However, certain combination of the exponents are much more reproducible – see the bottom lines of the table.

Table 4.1. Major critical exponents of continuous phase transitions

Exponents and combinations	Experimental range (3D) ^(a)	Mean-field theory	2D Ising model	3D Ising model	3D Heisenberg Model ^(d)
α	0 – 0.14	0 ^(b)	^(c)	0.12	-0.14
β	0.32 – 0.39	1/2	1/8	0.31	0.3
γ	1.3 – 1.4	1	7/4	1.25	1.4
δ	4-5	3	15	5	-
ν	0.6 – 0.7	1/2	1	0.64	0.7
ζ	0.05	0	1/4	0.05	0.04
$(\alpha + 2\beta + \gamma)/2$	1.00 ± 0.005	1	1	1	1
$\delta - \gamma/\beta$	0.93 ± 0.08	1	1	1	?
$(2 - \zeta)\nu/\gamma$	1.02 ± 0.05	1	1	1	1
$(2 - \alpha)/\nu d$	^(e)	4/d	1	1	1

^(a) Experimental data are from the monograph by A. Patashinskii and V. Pokrovskii, cited above.

^(b) Discontinuity at $\tau = 0$ – see below.

^(c) Instead of following Eq. (28), in this case C_h diverges as $\ln|\tau|$.

^(d) With the order parameter η defined as $\langle \sigma_j \cdot \mathbf{n}_B \rangle$.

^(e) I could not find any data on this.

Historically the first (and perhaps the most fundamental) of these *universal relations* was derived in 1963 by J. Essam and M. Fisher:

$$\alpha + 2\beta + \gamma = 2 . \quad (4.33)$$

It may be proved, for example, by finding the temperature dependence such magnetic field value, h_τ , which changes the order parameter by the amount similar to that already existing at $h = 0$, due to a finite temperature deviation $\tau > 0$. First, we may compare Eqs. (26) and (29), to get

$$h_\tau \propto \tau^{\beta+\gamma} . \quad (4.34)$$

By the physical sense of h_τ we may expect that such field has to affect system's free energy²⁴ $F(T, h)$ by the amount comparable to the effect of a bare temperature change τ . Ensemble-averaging the last term of Eq. (23) and using the definition (25) of the order parameter η , we see that the change of F (per particle) due to the field equals $-h_\tau \eta$ and, according to Eq. (26), scales as $h_\tau \tau^\beta \propto \tau^{(2\beta + \gamma)}$.

In order to estimate the thermal effect on F , let us first derive one more useful general thermodynamic formula.²⁵ Dividing Eq. (1.19) by dT , we may present heat capacity of a system as

$$C_X = T \left(\frac{\partial S}{\partial T} \right)_X, \quad (4.35)$$

where X is the variable maintained constant at the temperature variation. For example, in the standard “P-V” thermodynamics, we may use the first of Eqs. (1.35) to recast Eq. (35) for $X = V$ as

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V, \quad (4.36)$$

while for $X = P$ it may be combined with Eq. (1.39) to get

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_P. \quad (4.37)$$

As was just discussed, in the Ising model the role of pressure P is played by the external magnetic field h , and of G by F , so that the last form of Eq. (37) means that the thermal part of F may be found by double integration of $(-C_h/T)$ over temperature. In the context of our current discussion, this means that near T_c , the free energy scales as the double integral of $C_h \propto \tau^{-\alpha}$ over τ . In the limit $\tau \ll 1$, factor T may be treated as a constant; as a result, the change of F due to $\tau > 0$ alone scales as $\tau^{(2 - \alpha)}$. Requiring this change to be proportional to the same power of τ as the field-induced part of energy, we get the Essam-Fisher relation (33).

Using similar reasoning, it is straightforward to derive a few other universal relations of critical exponents, including the *Widom relation*,

²⁴ There is some duality of terminology (and notation) in literature on this topic. Indeed, in the Ising model (as in the Heisenberg model), the magnetic field effects are usually accounted at the microscopic level, by the inclusion of the corresponding term into each particular value of energy E_m . Then, as was discussed in Sec. 1.4, system's equilibrium (at fixed external field h , and also T and N) corresponds to the minimum of the *Helmholtz* free energy F . From this point of view, these problems do not feature either pressure or volume, hence we may take $PV = \text{const}$, so that both thermodynamic potentials effectively coincide: $G \equiv F + PV = F + \text{const}$. On the other hand, it is fair to say that the role of the magnetic field in these problems is very similar to that of pressure (or rather of $-P$) in the “usual” thermodynamics. Due to this analogy, and taking into account that the equilibrium of a system at fixed P corresponds to the minimum of the *Gibbs* free energy G , in some publications this name is used for the minimized potential. Still, on the microscopic level, there is a difference in the descriptions of field and pressure - see the footnote in the end of Sec. 2.4. Due to this reason, I will follow the traditional, first point of view in most of my narrative, but will use the replacements $F \rightarrow G$ and $h \rightarrow -P$ to use thermodynamic formulas (1.39) and (37) when convenient.

²⁵ Admittedly, it belongs to Chapter 1, but I was reluctant to derive it there to avoid a narrative interruption.

$$\delta - \frac{\gamma}{\beta} = 1, \quad (4.38)$$

very similar relations for other high-field exponents ε and μ (which I do not have time to discuss), and the *Fisher relation*

$$\nu(2 - \zeta) = \gamma. \quad (4.39)$$

A slightly more complex reasoning, involving the so-called *scaling hypothesis*, yields the dimensionality-dependent *Josephson relation*

$$\nu d = 2 - \alpha. \quad (4.40)$$

Table 1 shows that at least three of these relations are in a very reasonable agreement with experiment, so that we will use them as a testbed for various theoretical approaches to continuous phase transitions.

4.3. Landau's mean-field theory

The most general approach to analysis of the continuous phase transitions, formally not based on *any* particular model (though in fact implying the Ising model (23) or one of its siblings), is the *mean-field theory* developed in 1937 by L. Landau, on the basis of prior ideas by P.-E. Weiss - to be discussed in the next section. The main approximation of this phenomenological approach is to present the free energy change ΔF at the phase transition as an explicit function of the order parameter η (25). Generally this function may be complicated and model-specific, but near T_c , η has to tend to zero, so that the change of the relevant thermodynamic potential, the free energy,

$$\Delta F \equiv F(T) - F(T_c), \quad (4.41)$$

may be expanded into the Taylor series in η , and only a few, most important first terms of that expansion retained. In order to keep the symmetry between two possible signs of the order parameter in the absence of external field, at $h = 0$ this expansion should not include odd powers of η :

$$\frac{\Delta F}{V} \Big|_{h=0} = A(T)\eta^2 + \frac{1}{2}B(T)\eta^4 + \dots \quad (4.42)$$

As we will see imminently, these two terms are sufficient to describe finite (non-vanishing but limited) stationary values of the order parameter; this is why Landau's theory ignores the higher terms of the Taylor expansion - which are much smaller at $\eta \rightarrow 0$.

Now let us discuss temperature dependences of coefficients A and B . The equilibrium of the system should correspond to minimum of F . Equation (42) shows that, first of all, coefficient $B(T)$ has to be positive for any sign of τ , to ensure the equilibrium at a finite value of η^2 . Thus, it is reasonable to ignore the temperature dependence of B near the critical temperature altogether and use approximation

$$B(T) = b > 0. \quad (4.43)$$

On the other hand, as Fig. 6 shows, coefficient $A(T)$ has to change sign at $T = T_c$, being positive at $T > T_c$ and negative at $T < T_c$, to ensure the transition from $\eta = 0$ at $T > T_c$ to a certain non-vanishing value at $T < T_c$. Since A should be a smooth function of temperature, we may approximate it by the leading term in its Taylor expansion in τ :

$$A(T) = -a\tau, \quad \text{with } a > 0, \quad (4.44)$$

so that Eq. (42) becomes

$$\frac{\Delta F}{V} \Big|_{h=0} = -a\tau\eta^2 + \frac{1}{2}b\eta^4. \quad (4.45)$$

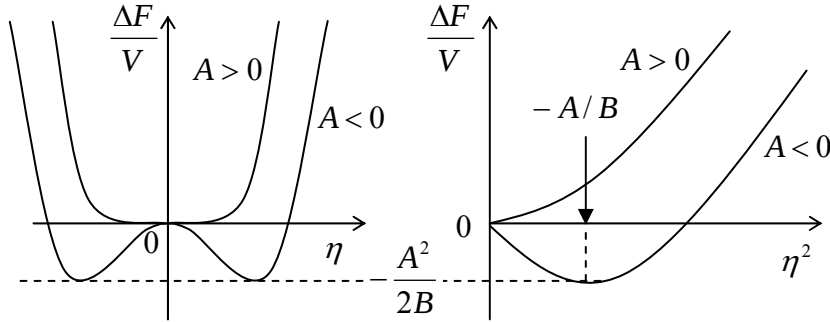


Fig. 4.6. Free energy (42) as a function of (a) η and (b) η^2 in Landau's mean-field theory, for two different signs of coefficient $A(\tau)$.

The main strength of Landau's theory is the possibility of its straightforward extension to the effects of the external field and of spatial variations of the order parameter. First, averaging of the field term of Eq. (23) over all sites of the system, with the account of Eq. (25), gives an energy addition of $-h\eta$ per particle, i.e. $-nh\eta$ per unit volume, where n is the particle density. Second, since (according to Eq. (23) with $\nu > 0$, see Table 1) the correlation radius diverges at $\tau \rightarrow 0$, spatial variations of the order parameter should be slow, $|\nabla\eta| \rightarrow 0$. Hence, the effects of the gradient on ΔF may be approximated by the first nonvanishing term of its expansion into the Taylor series in $(\nabla\eta)^2$. As a result, Eq. (45) may be generalized as

$$\Delta F = \int \Delta f d^3r, \quad \text{with } \Delta f = -a\tau\eta^2 + \frac{1}{2}b\eta^4 - nh\eta + c(\nabla\eta)^2, \quad (4.46)$$

where c is a factor independent of η . In order to avoid the unphysical effect of spontaneous formation of spatial variations of the order parameter, that factor has to be positive at all temperatures, and hence may be taken for constant in a small vicinity of T_c – the only region where Eq. (46) may be expected to provide quantitatively correct results.

Relation (46) is the full version of the free energy in Landau's theory.²⁶ Now let us find out what critical exponents are predicted by this phenomenological approach. First of all, we may find equilibrium values of the order parameter from the condition of F having a minimum, $\partial F/\partial\eta = 0$. At $h = 0$, it is easier to use the equivalent equation $\partial F/\partial(\eta^2) = 0$, where F is given by Eq. (45) – see Fig. 6b. This immediately yields

$$\eta = \begin{cases} (a\tau/b)^{1/2}, & \text{for } \tau > 0, \\ 0, & \text{for } \tau < 0. \end{cases} \quad (4.47)$$

²⁶ Historically, the last term belongs to the later (1950) extension of the theory by V. Ginzburg and L. Landau – see below.

Comparing this result with Eq. (26), we see that in the Landau theory, $\beta = 1/2$. Next, plugging result (47) back into Eq. (45), for the equilibrium (minimal) value of the free energy, we get

$$\Delta f = \begin{cases} -a^2 \tau^2 / 2b, & \text{for } \tau > 0, \\ 0, & \text{for } \tau < 0. \end{cases} \quad (4.48)$$

From here and Eq. (36), the specific heat,

$$\frac{C_h}{V} = \begin{cases} a^2 / bT_c, & \text{for } \tau > 0, \\ 0, & \text{for } \tau < 0, \end{cases} \quad (4.49)$$

has, at the critical point, a discontinuity rather than a singularity, i.e. the critical exponent $\alpha = 0$.

In the presence of a uniform field, the equilibrium order parameter should be found from the condition $\partial f / \partial \eta = 0$ applied to Eq. (46) with $\nabla \eta = 0$, giving

$$\frac{\partial f}{\partial \eta} \equiv -2a\tau\eta + 2b\eta^3 - nh = 0. \quad (4.50)$$

In the limit of small order parameter, $\eta \rightarrow 0$, term with η^3 is negligible, and Eq. (50) gives

$$\eta = -\frac{nh}{2a\tau}, \quad (4.51)$$

so that according to Eq. (29), $\gamma = 1$. On the other hand, at $\tau = 0$ (or at relatively high fields at other temperatures), the cubic term in Eq. (50) is much larger than the linear one, and this equation yields

$$\eta = \left(\frac{nh}{2b} \right)^{1/3}, \quad (4.52)$$

so that comparison with Eq. (32) yields $\delta = 3$.

Finally, according to Eq. (30), the last term in Eq. (46) scales as $c\eta^2/r_c^2$. (If $r_c \neq \infty$, the effects of the pre-exponential factor in that equation are negligible.) As a result, the gradient term contribution is comparable²⁷ with the two leading terms in Δf (which, according to Eq. (47), are of the same order), if

$$r_c \approx \left(\frac{c}{a|\tau|} \right)^{1/2}, \quad (4.53)$$

so that according to definition (31) of the critical exponent ν , it is equal to $1/2$.

The third column in Table 1 summarizes the critical exponents and their combinations in Landau's theory. It shows that these values are somewhat out of the experimental ranges, and while some of their universal relations are correct, some are not; for example, the Josephson relation would be only correct at $d = 4$ (not the most realistic spatial dimensionality :-). The main reason for this

²⁷ According to Eq. (30), the correlation radius may be interpreted as the length distance at which the order parameter η relaxes to its equilibrium value, if it is deflected from it at some point. Since the law of such spatial change may be obtained by a variational differentiation of F , for the actual relaxation law, all major terms of (46) have to be comparable.

disappointing result is that describing the spin interaction with the field, the Landau mean-field theory neglects spin randomness, i.e. fluctuations. Though a quantitative theory of thermodynamic fluctuations will not be discussed until the next chapter, we can readily perform their crude estimate. Looking at Eq. (46), we see that its first term is a quadratic function of the effective “half-degree of freedom”, η . Hence in accordance with the equipartition theorem (2.28) we may expect that the average square of its thermal fluctuations, within a d -dimensional volume with linear size $\sim r_c$, should be of the order of $T/2$ (close to the critical temperature, $T_c/2$ is a good approximation):

$$a|\tau|\langle\tilde{\eta}^2\rangle r_c^d \sim \frac{T_c}{2}. \quad (4.54)$$

In order to be negligible, the variance has to be negligible in comparison with the average $\eta^2 \sim a\tau/b$. Plugging in the τ -dependences of the operands of this relation, and values of the critical exponents in the Landau theory, for $\tau > 0$ we get the so-called *Levanyuk-Ginzburg criterion* of its validity:

$$\frac{T_c}{2a\tau} \left(\frac{a\tau}{c} \right)^{\frac{d}{2}} \ll \frac{a}{b} \tau. \quad (4.55)$$

We see that for any realistic dimensionality, $d < 4$, at $\tau \rightarrow 0$ the order parameter fluctuations grow faster than its average value, and hence the theory becomes invalid.

Thus the Landau mean-field theory is not a perfect approach to finding critical indices at continuous phase transitions in Ising-type systems with their next-neighbor interactions between the particles. Despite of that fact, this theory is very much valued because of the following reason. Any long-range interactions between particles increase the correlation radius r_c , and hence suppress the order parameter fluctuations. For an example, at laser self-excitation, the emerging coherent optical field couples *all* photon-emitting particles in the electromagnetic “cavity” (resonator). As another example, in superconductors the role of the correlation radius is played by the Cooper-pair size ξ_0 , which is typically of the order of 10^{-6} m, i.e. much larger than the average distance between the pairs ($\sim 10^{-8}$ m). As a result, the mean-field theory remains valid at all temperatures besides an extremely small temperature interval near T_c - for bulk superconductors, of the order of 10^{-6} K.

Another strength of Landau’s *classical* mean-field theory is that it may be readily generalized for description of Bose-Einstein condensates, i.e. *quantum* fluids. Of those generalizations, the most famous is the *Ginzburg-Landau theory* of superconductivity developed in 1950, i.e. even before the “microscopic” explanation of this phenomenon by Bardeen, Cooper and Schrieffer in the 1956-57. In the Ginzburg-Landau theory, the real order parameter η is replaced with the modulus of a complex function ψ , physically the wavefunction of the coherent Bose-Einstein condensate of Cooper pairs. Since each pair carry electric charge $q = -2e$,²⁸ and has zero spin, it interacts with magnetic field in a way different from that described by the Heisenberg or Ising models. Namely, as was already discussed in Sec. 3.4, the del operator ∇ in Eq. (46) has to be complemented by term $-i(q/\hbar)\mathbf{A}$, where $\mathbf{A}$ is the vector-potential of the total magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$, including not only the external magnetic field $\mathcal{H}$,

²⁸ In the phenomenological Ginzburg-Landau theory, charge q remains unspecified, though the wording in their original paper clearly shows that the authors correctly anticipated that this charge might turn out to be different from the single electron charge.

but also the field induced by the supercurrent itself. With the account for the well-known formula for the magnetic field energy in the external field,²⁹ Eq. (46) is now replaced with

$$\Delta f = -a\tau|\psi|^2 + \frac{1}{2}b|\psi|^4 - \frac{\hbar^2}{2m} \left| \left(\nabla - i \frac{q}{\hbar} \mathbf{A} \right) \psi \right|^2 + \frac{B^2}{2\mu_0} - \mathcal{H} \cdot \mathcal{B}, \quad (4.56)$$

Free
energy in
Ginzburg-
Landau
theory

where m is a phenomenological coefficient rather than the actual particle mass. The variational minimization of the resulting ΔF over variables ψ and $\mathbf{B}$ (which is suggested for reader's exercise³⁰) yields two differential equations:

$$\frac{\nabla \times \mathcal{B}}{\mu_0} = q \frac{i\hbar}{2m} \left[\psi \left(\nabla - i \frac{q}{\hbar} \mathbf{A} \right) \psi^* - \text{c.c.} \right], \quad (4.57)$$

Ginzburg-
Landau
equations

$$a\tau\psi = b|\psi|^2\psi - \frac{\hbar^2}{2m} \left(\nabla - i \frac{q}{\hbar} \mathbf{A} \right)^2 \psi. \quad (4.58)$$

The first of these *Ginzburg-Landau equations* should be no big surprise for the reader, because according to the Maxwell equations, in magnetostatics the left-hand part of Eq. (57) has to be equal to the electric current density, while the right-hand part is the usual quantum-mechanical probability current density multiplied by q , i.e. the electric current (or rather *supercurrent*) density $\mathbf{j}_s$ of the Cooper pair condensate. (Indeed, after plugging $\psi = n^{1/2} \exp\{i\varphi\}$ into that expression, we come back to Eq. (3.84) which, as we already know, explains such macroscopic quantum phenomena as magnetic flux quantization and Meissner-Ochsenfeld effect.)

However, Eq. (58) is new - for this course. Since last term in its right-hand part is the standard wave-mechanics expression for the kinetic energy of a particle in the presence of magnetic field,³¹ if this term dominates that part of the equation, Eq. (58) is reduced to the stationary Schrödinger equation, $E\psi = \hat{H}\psi$, for the ground state of confinement-free Cooper pairs, with energy $E = a\tau$. However, in contrast to the usual (single-particle) Schrödinger equation, in which $|\psi|$ is determined by the normalization condition, the Cooper pair condensate density $n = |\psi|^2$ is determined by the thermodynamic balance of the condensate with the ensemble of “normal” (unpaired) electrons that play the role of the uncondensed part of Bose gas, discussed in Sec. 3.4. In Eq. (58), such balance is enforced by the first term $b|\psi|^2\psi$ of the right-hand part.³² As we have already seen, in the absence of magnetic field and spatial gradients, such term yields $|\psi| \propto (T_c - T)^{1/2}$ – see Eq. (47).

²⁹ See, e.g., EM Eq. (5.129).

³⁰ As a useful elementary sanity check, the minimization of Δf in the absence of a superconductor, i.e. without the first 3 terms in the right-hand part of Eq. (56), immediately gives the correct result $\mathbf{B} = \mu_0 \mathbf{H}$.

³¹ See, e.g., QM Sec. 3.1.

³² From the mathematics standpoint, such term, nonlinear in $|\psi|$, makes Eq. (58) a member of the family of “nonlinear Schrödinger equations”. Another important member of this family is the *Gross-Pitaevskii equation*,

$$a\tau\psi = b|\psi|^2\psi - \frac{\hbar^2}{2m} \nabla^2 \psi + U(\mathbf{r})\psi,$$

which gives a very reasonable (albeit phenomenological and hence approximate) description of Bose-Einstein condensates of neutral atoms at $T \approx T_c$. The differences between the Ginzburg-Landau and Gross-Pitaevskii equations reflect, first, the zero charge q of the neutral atoms and, second, the fact that the atoms forming the

It is easy to see that as either the external magnetic field or the current density in a superconductor are increased, so is the last term in Eq. (58). This *increase* has to be matched by a corresponding *decrease* of $|\psi|^2$, i.e. of the condensate density n , until it is completely suppressed. This explains the well documented effect of superconductivity suppression by magnetic field and supercurrent. Moreover, together with the flux quantization discussed in Sec. 3.4, it explains the existence of the so-called *Abrikosov vortices* – thin tubes of magnetic field, each carrying one quantum Φ_0 of magnetic flux – see Eq. (3.86). At the core part of the vortex, $|\psi|^2$ is suppressed (down to zero at its central line) by the persistent supercurrent, which circulates around the core and screens the rest of superconductor from the magnetic field carried by the vortex. The penetration of such vortices into the so-called type-II superconductors³³ enables them to sustain vanishing electric resistance up to very high magnetic fields of the order of 20 T, and to be used in very compact magnets – including those used for beam bending in particle accelerators.

Moreover, generalizing Eq. (58) to the time-dependent case, just as it is done with the usual Schrödinger equation ($E \rightarrow i\hbar\partial/\partial t$), one can describe other fascinating quantum macroscopic phenomena such as the *Josephson effects*, including the generation of oscillations with frequency $\omega_J = (q/\hbar)\mathcal{V}$ by tunnel junctions between two superconductors, biased by dc voltage $\mathcal{V}$. Unfortunately, time/space restrictions do not allow me to discuss these effects in any detail here, and I have to refer the reader to special literature.³⁴ Let me only note that at $T \approx T_c$, and not extremely pure superconductors (in which the so-called non-local transport phenomena may be important), the Ginzburg-Landau equations are exact, and may be derived (and their parameters T_c , a , b , q , and m determined) from the “microscopic” theory of superconductivity based on the initial work by Bardeen, Cooper and Schrieffer.³⁵ Most importantly, such derivation proves that $q = -2e$ – the electric charge of a single Cooper pair.

4.4. Ising model: The Weiss’ molecular-field theory

The Landau mean-field theory is phenomenological in the sense that even within the range of its validity, it tells us nothing about the value of the critical temperature T_c and other parameters (in Eq. (46), a , b , and c), so that they have to be found from a particular “microscopic” model of the system under analysis. In this course, we would have time to discuss only the Ising model (23) for various dimensionalities d .

The most simplistic way to map the model on a mean-field theory is to assume that all spins are exactly equal, $s_j = \eta$, with an additional condition $\eta^2 \leq 1$, forgetting for a minute that in the genuine Ising model, s_j may equal only +1 or -1. Plugging this relation into Eq. (23), we get³⁶

condensates may be readily placed in external potentials $U(\mathbf{r}) \neq \text{const}$ (e.g., those trapping the atoms), while in superconductors such potential profiles are much harder to create due to the screening of electric field by metals – see, e.g., EM Sec. 2.1.

³³ Such penetration had been discovered experimentally by L. Shubnikov in the mid-1930s, but its quantitative explanation had to wait until A. Abrikosov’s work (based on the Ginzburg-Landau equations) published in 1957.

³⁴ See, e.g., M. Tinkham, *Introduction to Superconductivity*, 2nd ed., McGraw-Hill, 1996. A short discussion of the Josephson effects may be found in QM Sec. 2.3 and EM Sec. 6.4.

³⁵ See, e.g., Sec. 45 in E. Lifshitz and L. Pitaevskii, *Statistical Physics*, Part 2, Pergamon, 1980.

³⁶ Since in this naïve approach we neglect the thermal fluctuations of spin, i.e. their disorder, this assumption implies $S = 0$, so that $F \equiv E - TS = E$, and we may use either notation for system’s energy.

$$F = -(NJd)\eta^2 - Nh\eta. \quad (4.59)$$

This energy is plotted in Fig. 7a as a function of η , for several values of h . The plots show that at $h = 0$, the system may be in either of two stable states, with $\eta = \pm 1$, corresponding to two different directions of spins (magnetization), with equal energy.³⁷ (Formally, the state with $\eta = 0$ is also stationary, because at this point $\partial F/\partial \eta = 0$, but it is unstable, because for the ferromagnetic interaction, $J > 0$, the second derivative $\partial^2 F/\partial \eta^2$ is positive.)

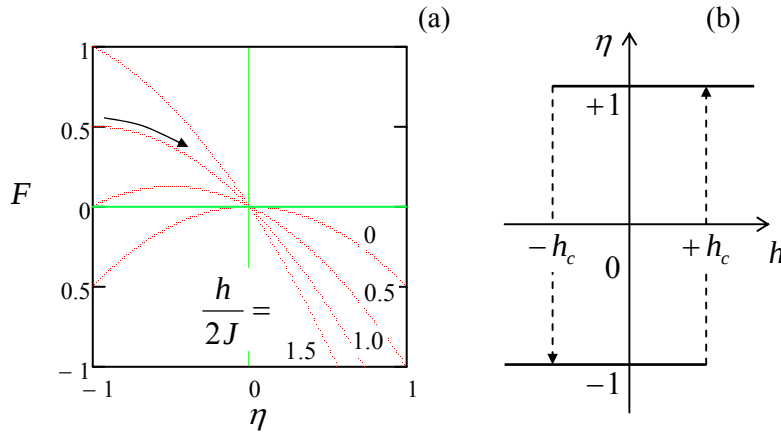


Fig. 4.7. Field dependence of (a) the free energy profile and (b) order parameter (i.e. magnetization) in the crudest mean-field approach to the Ising model.

As the external field is increased, it tilts the potential profile, and finally at a critical field,

$$h_c \equiv 2Jd, \quad (4.60)$$

the state with $\eta = -1$ becomes unstable, leading to system's jump into the only remaining state with opposite magnetization, $\eta = +1$. Application of the similar external field of the opposite polarity leads to the similar switching back to $\eta = -1$, so that the full field dependence of η follows the hysteretic pattern shown in Fig. 7b. Such a pattern is the most visible experimental feature of actual ferromagnetic materials, with the *coercitive magnetic field* $\mathcal{H}_c$ (modeled with h_c) of the order of 10^3 A/m, and the *saturated magnetization* (modeled with $\eta = \pm 1$) corresponding to much higher fields B - of the order of a few tesla. The most important property of these materials, also called *permanent magnets*, is their stability, i.e. the ability to retain the history-determined direction of magnetization in the absence of external field, for a very long time. In particular, this property is the basis of all magnetic systems for data recording, including the ubiquitous hard disk drives with their incredible information density - currently approaching 1 Terabit per square inch.³⁸

So, this simplest mean-field theory gives a crude description of the ferromagnetic ordering, but grossly overestimates the stability of these states with respect to thermal fluctuations. Indeed, in this

³⁷ The fact that stable states always correspond to $\eta = \pm 1$, partly justifies the treatment of η as a continuous variable in this crude approximation.

³⁸ For me, it was always surprising how little physics students knew about this fascinating field of modern engineering, which involves so much interesting physics and fantastic electromechanical technology. For getting acquainted with it, I may recommend, for example, the monograph by C. Mee and E. Daniel, *Magnetic Recording Technology*, 2nd ed., McGraw-Hill, 1996.

theory, there is no thermally-induced randomness at all, until T becomes comparable with the height of the energy barrier separating two stable states,

$$\Delta F \equiv F(\eta = 0) - F(\eta = \pm 1) = NJd, \quad (4.61)$$

which is proportional to the number of particles. At $N \rightarrow \infty$, this value diverges, and in this sense the critical temperature is infinite, while numerical experiments and more refined theories of the Ising model show that actually the ferromagnetic phase is suppressed at $T_c \sim Jd$ – see below.³⁹

The mean-field approach may be dramatically improved by even an approximate account for thermally-induced randomness. In this approach, suggested in 1908 by P.-E. Weiss under the name of *molecular-field theory*,⁴⁰ random deviations of individual spin values from the lattice average,

$$\tilde{s}_j \equiv s_j - \eta, \quad \eta \equiv \langle s_j \rangle, \quad (4.62)$$

are allowed, but considered small, $|\tilde{s}_j| \ll \eta$. This assumption allows us, after plugging expression $s_j = \eta + \tilde{s}_j$ into the first term of the right-hand part of Eq. (23),

$$E_m = -J \sum_{\langle j, j' \rangle} (\eta + \tilde{s}_j)(\eta + \tilde{s}_{j'}) - h \sum_j s_j, \quad (4.63)$$

ignore the term proportional to $\tilde{s}_j \tilde{s}_{j'}$. Making replacement (62) in the terms proportional to $\tilde{s}_j$, we get

$$E_m \rightarrow E_m' \equiv (NJd)\eta^2 - h_{\text{ef}} \sum_j s_j, \quad (4.64)$$

where h_{ef} is defined as the sum

$$h_{\text{ef}} \equiv h + (2Jd)\eta. \quad (4.65)$$

The physical interpretation of h_{ef} is the *effective* external field, which (besides the real external field h) takes into account the effect that *would be* exerted on spin s_j by its $2d$ next neighbors, if they all had unperturbed (but possibly fractional) spins $s_j = \eta$. Such an addition to external field,

$$h_{\text{mol}} \equiv h_{\text{ef}} - h = (2Jd)\eta, \quad (4.66)$$

is called the *molecular field* - giving its name to the theory.

From the point of view of statistical physics, at fixed parameters of the system (including the order parameter η), the first term in the right-hand part of Eq. (64) is merely a constant energy offset, and h_{ef} is just another constant, so that

$$E_m' = \text{const} + \sum_j E_j, \quad E_j = -h_{\text{ef}} s_j = \begin{cases} -h_{\text{ef}}, & \text{for } s_j = +1, \\ +h_{\text{ef}}, & \text{for } s_j = -1. \end{cases} \quad (4.67)$$

³⁹ Actually, the thermal stability of many real ferromagnets, with longer-range interaction between spins, is higher than that predicted by the Ising model.

⁴⁰ In some texts, this approximation is called the mean-field theory. This terminology may lead to confusion, because the molecular-field theory is on a completely different level of phenomenology than, say, Landau's mean-field theory. For example, the molecular-field approach may be used for the calculation of parameters a , b , and T_c participating Eq. (46) - the starting point of Landau's theory.

Such separability of energies means that in the Weiss approximation the spin fluctuations are independent, and their statistics may be examined individually, using energy spectrum E_j . But this is exactly the two-level system which was the subject of three exercise problems in Chapter 2. Actually, its statistics is so simple that it is easier to redo this fundamental problem starting from scratch, rather than to use the results of those exercises (which would require changing notation). Indeed, according to the Gibbs distribution (2.58)-(2.59), the equilibrium probabilities of states $s_j = \pm 1$ may be found as

$$W_{\pm} = \frac{1}{Z} e^{\pm h_{\text{ef}}/T}, \quad Z = \exp\left\{+\frac{h_{\text{ef}}}{T}\right\} + \exp\left\{-\frac{h_{\text{ef}}}{T}\right\} = 2 \cosh \frac{h_{\text{ef}}}{T}. \quad (4.68)$$

From here, we may readily calculate $F = -T \ln Z$ and other thermodynamic variables, but let us immediately use Eq. (68) to calculate the statistical average of s_j , i.e. the order parameter:

$$\eta \equiv \langle s_j \rangle = (+1)W_+ + (-1)W_- = \frac{e^{+h_{\text{ef}}/T} - e^{-h_{\text{ef}}/T}}{2 \cosh(h_{\text{ef}}/T)} = \tanh \frac{h_{\text{ef}}}{T}. \quad (4.69)$$

Now comes the main trick of the Weiss' approach: plugging this result back into Eq. (65), we may write the condition of *self-consistency* of the molecular field theory:

$$h_{\text{ef}} - h = 2Jd \tanh \frac{h_{\text{ef}}}{T}. \quad (4.70)$$

Self-consistency equation

This is a transcendent equation that evades an explicit analytical solution, but its properties may be readily understood by plotting its both parts as functions of their argument, so that the stationary state(s) of the system corresponds to the intersection point(s) of these plots.

First of all, let us explore the field-free case ($h = 0$), when $h_{\text{ef}} = h_{\text{mol}} \equiv 2dJ\eta$, so that Eq. (70) is reduced to

$$\eta = \tanh\left(\frac{2Jd}{T} \eta\right), \quad (4.71)$$

giving one of the patterns sketched in Fig. 8, depending on the dimensionless parameter $2Jd/T$.

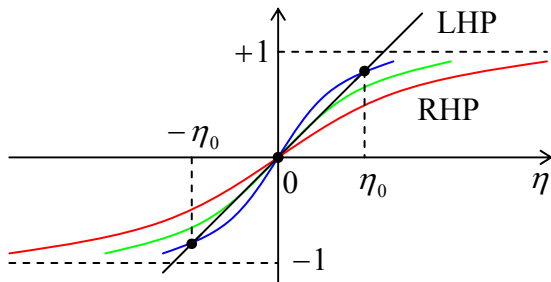


Fig. 4.8. Ferromagnetic phase transition in Weiss' molecular-field theory: two sides of Eq. (71) plotted as functions of η for 3 temperatures: above T_c (red), below T_c (blue) and equal to T_c (green).

If this parameter is small, the right-hand part of Eq. (71) grows slowly with η (red line in Fig. 8), and there is only one intersection point with the left-hand part plot, at $\eta = 0$. This means that the spin system features no spontaneous magnetization – the so-called *paramagnetic phase*. However, if parameter $2Jd/T$ exceeds 1, i.e. T is decreased below the following critical value,

Critical
("Curie")
temperature

$$T_c = 2Jd, \quad (4.72)$$

the right-hand part grows, at small η , faster than the left-hand part, so that their plots intersect it in 3 points: $\eta = 0$ and $\eta = \pm\eta_0$. It is almost evident that the former stationary point is unstable while two latter points are stable.⁴¹ Thus, below T_c the system is in the ferromagnetic phase, with one of two possible directions of spontaneous magnetization, so that the critical (Curie) temperature, given by Eq. (72), marks the transition between the paramagnetic and ferromagnetic phases. (Since the stable minimum value of energy G is a continuous function of temperature at $T = T_c$, this is the continuous phase transition.)

Now let us repeat the same graphics to examine how each of these phases responds to external magnetic field $h \neq 0$. According to Eq. (70), the effect of h is just a shift of the straight line plot of its left-hand part – see Fig. 9.

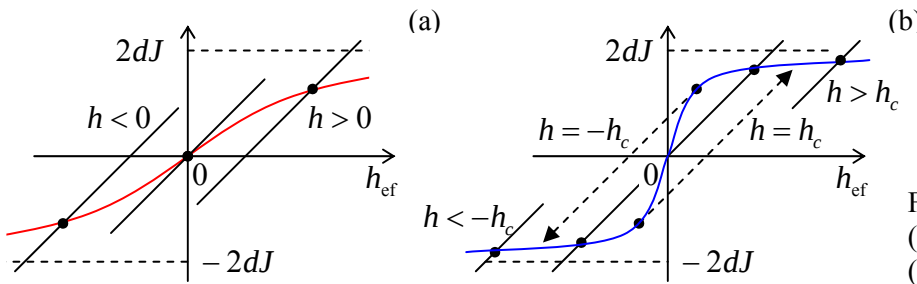


Fig. 4.9 External field effect on:
(a) a paramagnet ($T > T_c$), and
(b) a ferromagnet ($T < T_c$).

In the paramagnetic case (Fig. 9a) the resulting dependence $h_{\text{ef}}(h)$ is evidently continuous, but the coupling effect ($J > 0$) makes it more steep than it would be without spin interaction. This effect may be characterized by the low-field susceptibility defined by Eq. (29). To calculate it, let us notice that for small h , and hence h_{ef} , function $\tanh$ in Eq. (70) is approximately equal to argument, so that Eq. (70) becomes

$$h_{\text{ef}} - h = \frac{2Jd}{T} h_{\text{ef}}. \quad (4.73)$$

Solving this equation for h_{ef} , and then using Eq. (72), we get

$$h_{\text{ef}} = \frac{h}{1 - 2Jd/T} = \frac{h}{1 - T_c/T}. \quad (4.74)$$

Recalling Eq. (66), we can rewrite this result for the order parameter,

$$\eta = \frac{h_{\text{ef}} - h}{T_c} = \frac{h}{T - T_c}, \quad (4.75)$$

meaning that the low-field susceptibility

⁴¹ This fact may be readily verified by using Eqs. (64) and (68) to calculate F . Now condition $\partial F / \partial \eta|_{h=0} = 0$ returns us to Eq. (71), and calculating the second derivative, for $T < T_c$ we get $\partial^2 F / \partial \eta^2 > 0$ at $\eta = \pm\eta_0$ (indicating two stable minima of F), and $\partial^2 F / \partial \eta^2 < 0$ at $\eta = 0$ (the unstable maximum of F).

$$\chi \equiv \frac{\partial \eta}{\partial h} \Big|_{h=0} = \frac{1}{T - T_c}, \quad \text{for } T > T_c. \quad (4.76)$$

Curie-Weiss law

This is the famous *Curie-Weiss law*, which shows that the susceptibility diverges at the approach to the Curie temperature T_c .

In the ferromagnetic case, the graphic solution (Fig. 9b) of Eq. (70) gives a qualitatively different result. A field increase leads, depending on the spontaneous magnetization, either the further saturation of h_{mol} (with the order parameter η gradually approaching 1), or, if the initial η was negative, a jump to positive η at some critical (coercitive) field h_c . In contrast with the crude mean-field approximation (59), at $T > 0$ the coercitive field is smaller than that given by Eq. (60), and the magnetization saturation is gradual, in a good (semi-qualitative) accordance with experiment.

To summarize, the Weiss' molecular-field theory gives a more realistic description of the ferromagnetic and paramagnetic phases in the Ising model, and a very simple prediction (72) of the temperature of the phase transition between them, for an arbitrary dimensionality d of the cubic lattice. It also allows finding all other parameters of the mean-field theory for that model – an easy exercise left for the reader.

4.5. Ising model: Exact and numerical results

In order to evaluate the main prediction (72) of the Weiss theory, let us now discuss the exact (analytical) and quasi-exact (numerical) results obtained for the Ising model, going from the lowest dimensionality $d = 0$ to its higher values.

Zero dimensionality means that a spin has no nearest neighbors at all, so that the first term of Eq. (23) vanishes. Hence Eq. (64), with $h_{\text{ef}} = h$, is exact, and so is its solution (69). Now we can repeat the calculations that have led us to Eq. (76), with $J = 0$, i.e. $T_c = 0$, and reduce this result to the so-called *Curie law*:

$$\chi = \frac{1}{T}. \quad (4.77)$$

Curie law

It shows that $T_c = 0$, i.e. the system is paramagnetic at any temperature. One may say that for this case the Weiss molecular-field theory is exact - or in some sense trivial, because it provides an exact, fully quantum-mechanical treatment of spin- $\frac{1}{2}$ particles at negligible interaction. Experimentally, the Curie law is approximately valid for many so-called *paramagnetic materials*, i.e. 3D systems with a weak interaction between particle spins.

The case $d = 1$ is more complex, but has an exact analytical solution. Probably the simplest way to obtain it is to use the so-called *transfer matrix approach*.⁴² For this, first of all, we may argue that properties of a 1D system of $N \gg 1$ spins (say, put at equal distances on a straight line) should not change noticeably if we bend that line gently into a closed loop (Fig. 10), i.e. assume that spins s_1 and s_N form one more pair of next neighbors, giving one more contribution, $-Js_1s_N$, to energy (23):

$$E_m = -(Js_1s_2 + Js_2s_3 + \dots + Js_Ns_1) - (hs_1 + hs_2 + \dots + hs_N). \quad (4.78)$$

⁴² It was developed in 1941 by H. Kramers and G. Wannier. Note that the approach is very close to the one used in 1D quantum mechanics – see, e.g., QM Sec. 2.5.

Let us regroup terms of this sum in the following way:

$$E_m = - \left[\left(\frac{h}{2} s_1 + J s_1 s_2 + \frac{h}{2} s_2 \right) + \left(\frac{h}{2} s_2 + J s_2 s_3 + \frac{h}{2} s_3 \right) + \dots + \left(\frac{h}{2} s_N + J s_N s_1 + \frac{h}{2} s_1 \right) \right], \quad (4.79)$$

so that the group in each parentheses depends only on the state of two adjacent spins. The corresponding statistical sum,

$$Z = \sum_{\substack{s_j = \pm 1 \\ j=1,2,\dots,N}} \exp \left\{ h \frac{s_1}{2T} + J \frac{s_1 s_2}{T} + h \frac{s_2}{2T} \right\} \exp \left\{ h \frac{s_2}{2T} + J \frac{s_2 s_3}{T} + h \frac{s_3}{2T} \right\} \dots \exp \left\{ h \frac{s_N}{2T} + J \frac{s_N s_1}{T} + h \frac{s_1}{2T} \right\}, \quad (4.80)$$

has 2^N terms, each corresponding to a certain combination of signs of N spins. Each operand of the product under the sum may take 4 values for 4 different combinations of its two arguments:

$$\exp \left\{ h \frac{s_j}{2T} + J \frac{s_j s_{j+1}}{T} + h \frac{s_{j+1}}{2T} \right\} = \begin{cases} \exp\{(J+h)/T\}, & \text{for } s_j = s_{j+1} = +1, \\ \exp\{(J-h)/T\}, & \text{for } s_j = s_{j+1} = -1, \\ \exp\{-J/T\}, & \text{for } s_j = -s_{j+1}. \end{cases} \quad (4.81)$$

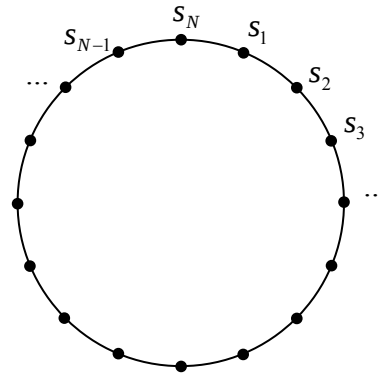


Fig. 4.10. 1D Ising system on a circular loop.

These values do not depend on index j ,⁴³ and may be presented as elements of the so-called *transfer matrix*

$$M = \begin{pmatrix} \exp\{(J+h)/T\} & \exp\{-J/T\} \\ \exp\{-J/T\} & \exp\{(J-h)/T\} \end{pmatrix}, \quad (4.82)$$

and the whole statistical sum may be recast as a product:

$$Z = \sum_{\substack{s_j = \pm 1 \\ j=1,2,\dots,N}} M_{s_1 s_2} M_{s_2 s_3} \dots M_{s_N s_1}. \quad (4.83)$$

According to the basic rule of matrix multiplication, this sum is just

⁴³ This is of course a result of the “translational” (or rather rotational) symmetry of the system, i.e. its invariance to the index replacement $j \rightarrow j+1$ in all terms of energy H_m (besides index N which should be replaced with 1).

$$Z = \text{Tr}(\mathbf{M}^N). \quad (4.84)$$

Matrix algebra tells us that this trace may be presented just as

$$Z = \lambda_+^N + \lambda_-^N \quad (4.85)$$

where $\lambda_{\pm}$ are the eigenvalues of the transfer matrix $\mathbf{M}$, i.e. the roots of its characteristic equation,

$$\begin{vmatrix} \exp\{(J+h)/T\} - \lambda & \exp\{-J/T\} \\ \exp\{-J/T\} & \exp\{(J-h)/T\} - \lambda \end{vmatrix} = 0. \quad (4.86)$$

A straightforward calculation yields

$$\lambda_{\pm} = \exp\left\{\frac{J}{T}\right\} \left[\cosh \frac{h}{T} \pm \left(\sinh^2 \frac{h}{T} + \exp\left\{-\frac{4J}{T}\right\} \right)^{1/2} \right]. \quad (4.87)$$

Now the last simplification comes from condition $N \gg 1$ - which we needed anyway, to make the loop model equivalent to an infinite 1D system. In this limit, even a small difference of exponents, $\lambda_+ > \lambda_-$, makes the second term in Eq. (85) negligible, so that we finally get

$$Z = \lambda_+^N = \exp\left\{\frac{NJ}{T}\right\} \left[\cosh \frac{h}{T} + \left(\sinh^2 \frac{h}{T} + \exp\left\{-\frac{4J}{T}\right\} \right)^{1/2} \right]^N. \quad (4.88)$$

From here, we can find the free energy per particle

$$\frac{F}{N} = \frac{T}{N} \ln \frac{1}{Z} = -J - T \ln \left[\cosh \frac{h}{T} + \left(\sinh^2 \frac{h}{T} + \exp\left\{-\frac{4J}{T}\right\} \right)^{1/2} \right], \quad (4.89)$$

and hence can calculate all variables of interest from thermodynamic relations. In particular, the equilibrium value of the order parameter may be found from the last of Eqs. (1.39), with the replacements discussed above: $G \rightarrow F$, $P \rightarrow -h$, and hence $V = (\partial G / \partial P)_T \rightarrow -(\partial F / \partial h)_T = N\eta$. For low fields ($h \ll T$), this formula yields

$$\eta = \frac{h}{T} \exp\left\{\frac{2J}{T}\right\}. \quad (4.90)$$

This result describes linear magnetization with the following low-field susceptibility,

$$\chi \equiv \frac{\partial \eta}{\partial h} \Big|_{h=0} = \frac{1}{T} \exp\left\{\frac{2J}{T}\right\}, \quad (4.91)$$

and means that the 1D Ising model does *not* exhibit a phase transition, i.e., $T_c = 0$. However, its susceptibility grows, at $T \rightarrow 0$, much faster than the Curie law (77). This gives us a hint that at low temperatures the system is “virtually ferromagnetic”, with has the ferromagnetic order with some rare violations. (In physics, such violations are called low-temperature *excitations*.) This perception may be confirmed by the following approximate calculation.

It is almost evident that the lowest-energy excitation of a 1D ferromagnet at $h = 0$ is the reversal of signs of all spins in one of its parts (Fig. 11). Indeed, since such excitation (called the *Bloch wall*)

involves the change of sign of just one product $s_j s_{j'}$, according to Eq. (78), its energy E_W (defined as the difference between values of E_m with and without the excitation) equals $2J$, regardless of the wall position. Since in a ferromagnet, parameter J is positive, $E_W > 0$. If the system tried to minimize its potential energy, having any wall in the system would be energy-disadvantageous. However, thermodynamics tells us that at finite T , system's equilibrium corresponds to the minimum of free energy rather than just energy.⁴⁴ Hence, we have to calculate Bloch wall's contribution E_W to the free energy. Since in a linear chain of $N \gg 1$ spins, the wall can take $(N - 1) \approx N$ positions with the same energy E_W , we may claim that the entropy S_W associated with an excitation of this type is $\ln N$, and its according to definition (1.33) of the free energy,

$$F_W = E_W - TS_W \approx 2J - T \ln N. \quad (4.92)$$

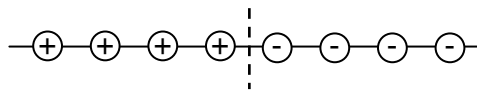


Fig. 4.11. A Bloch wall in a 1D Ising system.

This result tells us that in the limit $N \rightarrow \infty$, and at $T \neq 0$, walls are always free-energy-beneficial, thus explaining the absence of the perfect ferromagnetic order in the 1D Ising system. Note, however, that since the logarithm grows extremely slowly at large values of its argument, one may argue that a large but finite 1D system would still feature a quasi-critical temperature

$$T_c = \frac{2J}{\ln N}, \quad (4.93)$$

below which it would feature a virtually complete ferromagnetic order. (The exponentially large susceptibility (91) is a manifestation of this fact.)

Now let us apply a similar approach to estimate T_c of a 2D Ising model. Here the Bloch wall is a line of certain length L – see Fig. 12. (For this example, counting from the left to the right, $L = 2 + 1 + 4 + 2 + 3 = 12$ lattice periods.)

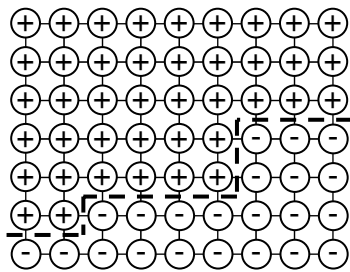


Fig. 4.12. A Bloch wall in a 2D Ising system.

Evidently, the additional energy associated with such wall is $E_W = 2JL$, while wall's entropy may be estimated approximately using the following reasoning. Let the wall be formed by the path of a “Manhattan pedestrian” traveling through the lattice between its nodes. At each junction, the pedestrian

⁴⁴ If the reader is still uncomfortable with this core result of thermodynamics, he or she is strongly encouraged to revisit Eq. (1.43) and its discussion.

may select 3 choices of 4 directions (except the one that leads backward), so that there are approximately $3^{(L-1)}$ options for a walk starting from a certain point, i.e. approximately $M \sim 2(N-1)^{1/2} \times 3^L \approx 2N^{1/2} 3^L$ different walks starting from two sides of a square-shaped lattice (of linear size $N^{1/2}$). Again calculating S_W as $\ln M$, we get

$$F_W = E_W - TS_W \approx 2JL - T \ln(2N^{1/2} \times 3^L) = L(2J - T \ln 3) - T \ln(2N^{1/2}). \quad (4.94)$$

Since L scales as $N^{1/2}$ or higher, at $N \rightarrow \infty$ the last term is negligible, and we see that sign of $\partial F_W / \partial L$ depends on whether the temperature is higher or lower than the following critical value

$$T_c = \frac{2}{\ln 3} J \approx 1.82 J. \quad (4.95)$$

At $T < T_c$, the Free energy minimum corresponds to $L \rightarrow 0$, i.e. Bloch walls are free-energy-beneficial, and the system is in the ferromagnetic phase.

So, for $d = 2$ the estimates predict a finite critical temperature of the same order as the Weiss' theory ($T_c = 4J$). The major approximation in the calculation leading to Eq. (95) is disregarding possible self-crossing of the “Manhattan walk”. An accurate counting of such self-crossings is rather difficult. It had been carried out in 1944 by L. Onsager; since then his calculations have been redone in several easier ways, but even they are rather cumbersome, and I will not have time to discuss them in detail.⁴⁵ The final result, however, is surprisingly simple:

$$\tanh \frac{J}{T_c} = \sqrt{2} - 1, \quad \text{giving } T_c \approx 2.269 J, \quad (4.96)$$

Onsager's
result

i.e. showing that the simple estimate (95) is only ~20% off the mark.

The Onsager solution, as well as all alternative solutions of the problem that were found later, are so “artificial” (2D-specific) that they do not give a clear clue to their generalization to other (higher) dimensions. As a result, the 3D Ising problem is still unsolved analytically. Nevertheless, we do know T_c for that case with an extremely high precision – at least to the 6th decimal place. This has been achieved by numerical methods; they deserve a thorough discussion, are applicable to other problems as well. Conceptually, this task is rather simple: just compute, to the desired precision, the statistical sum of system (23):

$$Z = \sum_{\substack{s_j = \pm 1 \\ j=1,2,\dots,N}} \exp \left\{ \frac{J}{T} \sum_{\{j,j'\}} s_j s_{j'} + \frac{h}{T} \sum_j s_j \right\}. \quad (4.97)$$

As soon as this has been done for a sufficient number of values of dimensionless parameters J/T and h/T , everything else is easy; in particular, we can compute the dimensionless function

$$F/T = -\ln Z, \quad (4.98)$$

and then find the ratio J/T_c as the smallest value of parameter J/T , at that F/T (as a function of ratio h/T) has a minimum at zero field. However, for any system of a reasonable size N , the “exact” computation of the statistical sum (97) is impossible, because it contains too many terms for any supercomputer to

⁴⁵ For that, the reader is referred to either Sec. 151 in the textbook by Landau and Lifshitz or Chapter 15 in the text by Huang, both cited above.

handle. For example, let us take a relatively small 3D lattice with $N = 10 \times 10 \times 10 = 10^3$ spins, which still feature substantial boundary effects even using the periodic boundary conditions (similar to the Born-Karman conditions in the wave theory), so that its phase transition is smeared about T_c by $\sim 1\%$. Still, even for that crude model, Z would include $2^{1,000} = (2^{10})^{100} \approx (10^3)^{100} = 10^{300}$ terms. Let us suppose we are using a prospective exaflops-scale computer performing 10^{18} floating-point operations per second, i.e. $\sim 10^{26}$ such operations per year. With those resources, the computation of just one statistical sum would require $\sim 10^{(300-26)} = 10^{274}$ years. To call such number “astronomic” would be a strong understatement. (As a reminder, the age of our Universe is believed to be close to 1.3×10^{10} years – a very humble number in comparison.)

This situation may be improved dramatically by noticing that any statistical sum,

$$Z = \sum_m \exp\left\{-\frac{E_m}{T}\right\}, \quad (4.99)$$

is dominated by terms with lower values of E_m . In order to find those lowest-energy states, we may use the following powerful approach (belonging to a broad class of *Monte-Carlo techniques*), which essentially mimics one (randomly selected) path of system’s evolution in time. One could argue that for that we would need to know the exact laws of evolution of statistical systems,⁴⁶ that may differ from one system to another, even if their energy spectra E_m are the same. This is true, but since the equilibrium value of Z should be independent of these details, it may be evaluated using *any* kinetic model, provided that it satisfies certain general rules. In order to reveal these rules, let us start from a system with just two states, E_m and $E_{m'} = E_m + \Delta$ – see Fig. 13.

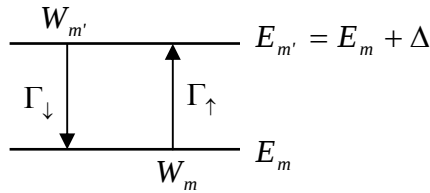


Fig. 4.13. Deriving the detailed balance equation.

In the absence of quantum coherence between the states (see Sec. 2.1), equations for time evolution of the corresponding probabilities W_m and $W_{m'}$ should depend only on the probabilities (plus certain constant coefficients). Moreover, since equations of quantum mechanics are linear, the equations of probability evolution should be also linear. Hence, it is natural to expect them to have the following form,

$$\frac{dW_m}{dt} = W_{m'}\Gamma_{\downarrow} - W_m\Gamma_{\uparrow}, \quad \frac{dW_{m'}}{dt} = W_m\Gamma_{\uparrow} - W_{m'}\Gamma_{\downarrow}, \quad (4.100)$$

where constant coefficients $\Gamma_{\uparrow}$ and $\Gamma_{\downarrow}$ have the physical sense of *rates* of the corresponding transitions – see Fig. 13. According to the *master equations* (100) the rates have simple meaning: for example, $\Gamma_{\uparrow}dt$ is the probability of the system’s transition into state m' during an infinitesimal time interval dt , provided that in the beginning of that interval it was in state m with full certainty: $W_m = 1, W_{m'} = 0$.⁴⁷

⁴⁶ Discussion of such laws in the task of *physical kinetics*, which will be briefly reviewed in Chapter 6.

⁴⁷ The calculation of these rates for several particular cases is described in QM Secs. 6.6, 6.7, and 7.6.

Since for the system with just two energy levels, the time derivatives of the probabilities are equal and opposite, Eqs. (100) describe an (irreversible) redistribution of the probabilities while keeping their sum $W = W_m + W_{m'}$ constant. At $t \rightarrow \infty$, $d/dt \rightarrow 0$, and the probabilities settle to their stationary values related as

$$\frac{W_{m'}}{W_m} = \frac{\Gamma_{\uparrow}}{\Gamma_{\downarrow}}. \quad (4.101)$$

Now let us require that these stationary values obey the Gibbs distribution (2.58); then

$$\frac{W_{m'}}{W_m} = \exp\left\{\frac{E_m - E_{m'}}{T}\right\} = \exp\left\{-\frac{\Delta}{T}\right\} < 1. \quad (4.102)$$

Comparing these two expressions, we see that the rates have to satisfy the following *detailed balance* relation

$$\boxed{\frac{\Gamma_{\uparrow}}{\Gamma_{\downarrow}} = \exp\left\{-\frac{\Delta}{T}\right\}}. \quad (4.103) \quad \text{Detailed balance relation}$$

By the way, this relation may serve as an important sanity check: the rates calculated using any reasonable model of a quantum system have to satisfy it.⁴⁸

Now comes the final argument: since the rates of transition between two particular states should not depend on other states and their occupation, Eq. (103) has to be valid for *each* pair of states of any multi-state system. The detailed balance yields only one equation for two rates $\Gamma_{\uparrow}$ and $\Gamma_{\downarrow}$; if our only goal is the calculation of Z , the choice of the other equation is not too important. Perhaps the simplest choice is

$$\Gamma(\Delta) \propto \gamma(\Delta) \equiv \begin{cases} 1, & \text{if } \Delta < 0, \\ \exp\{-\Delta/T\}, & \text{otherwise,} \end{cases} \quad (4.104)$$

where Δ is the energy change resulting from the transition. This model, which evidently satisfies the detailed balance relation (103), is the most popular for its simplicity, despite the unphysical cusp this function has at $\Delta = 0$. The simplicity of Eq. (104) enables the following *Metropolis algorithm* (Fig. 14). The calculation starts from setting a certain initial state of the system. At relatively high temperatures, the state may be generated randomly; for example, for the Ising system, the initial state of each spin s_j may be selected independently, with the 50% probability. At low temperatures, starting the calculations from the lowest-energy state (in particular, for the Ising model, from the ferromagnetic state $s_j = \text{sgn}(h) = \text{const}$) may give the fastest convergence of the sum (97).

Now one spin is flipped at random, and the corresponding change of energy (Δ) is calculated,⁴⁹ and plugged into Eq. (104) to calculate $\gamma(\Delta)$. Next, a pseudo-random number generator is used to generate a random number ξ , with the probability density uniformly distributed on segment $[0, 1]$. (Such

⁴⁸ See, e.g., QM Eq. (7.196) for a quantum system bilinearly coupled to an environment in thermal equilibrium. By the way, that formula (as well as results for all realistic physical systems) does not feature the unphysical cusp of function $\Gamma(\Delta)$ at $\Delta = 0$, assumed by the popular model (104).

⁴⁹ Note that the flip changes signs of only $(2d + 1)$ terms in sum (23), i.e. does not require re-calculation of all $(2d + 1)N$ terms of the sum, so that the computation of Δ takes just a few add-multiply operations even at $N \gg 1$.

functions, typically called RND, are available in virtually any numerical library.) If the resulting ξ is less than $\gamma(\Delta)$, the transition is accepted, while if $\xi > \gamma(\Delta)$, it is rejected. In the view of Eq. (104), this means that any transition down the energy spectrum ($\Delta < 0$) are always accepted, while those up the energy profile ($\Delta > 0$) are accepted with the probability proportional to $\exp\{-\Delta/T\}$. The latter feature is necessary to avoid system trapping in local minima of its multidimensional energy profile $E_m(s_1, s_2, \dots, s_N)$. Now the statistical sum may be calculated approximately as a partial sum over the states passed by the system. (It is better to discard the contributions from a few first steps to avoid an error due to the initial state choice.)

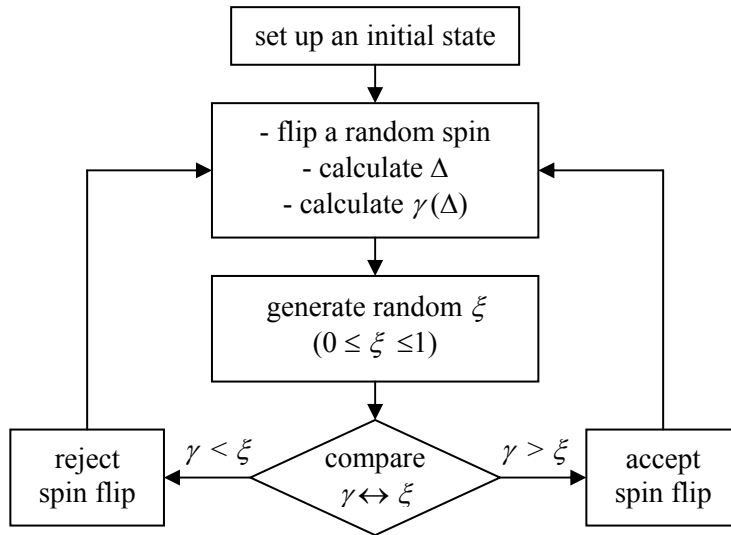


Fig. 4.14. Crude scheme of the Monte Carlo algorithm for the Ising model simulation.

This algorithm is extremely efficient. Even with modest computers available in the 1980s, it has allowed to simulate a 3D Ising system of $(128)^3$ spins to get the following result: $J/T_c \approx 0.221650 \pm 0.000005$. For all practical purposes, this result is exact (so that perhaps the largest benefit of the possible analytical solution for the infinite 3D Ising system would be a virtually certain Nobel Prize for the author :-). Table 2 summarizes values of T_c for the Ising model. Very visible is the fast improvement of prediction accuracy of the molecular-field theory - which is asymptotically correct at $d \rightarrow \infty$.

Table 2. Critical temperature T_c (in the units of J) of the Ising model of a ferromagnet ($J > 0$) for several values of dimensionality d

d	Molecular-field theory - Eq. (72)	Exact value	Exact value's source
0	0	0	Gibbs distribution
1	2	0	Transfer matrix theory
2	4	2.269...	Onsager's solution
3	6	4.513...	Numerical simulation

Finally, I need to mention the *renormalization-group* (“RG”) approach,⁵⁰ despite its low efficiency for the Ising problem. The basic idea of this approach stems from the scaling law (30)-(31): at $T = T_c$ the correlation radius r_c diverges. Hence, the critical temperature may be found from the requirement for the system to be *spatially self-similar*. Namely, let us form larger and larger groups (“blocks”) of adjacent spins, and require that all properties of the resulting system of the blocks approach those of the initial system, as T approaches T_c .

Let us see how does this idea work for the simplest nontrivial (1D) case, which is described by statistical sum (80). Assuming N to be even (which does not matter at $N \rightarrow \infty$), and adding an inconsequential constant C to each exponent (for the purpose that will be clear later on), we may rewrite this expression as

$$Z = \sum_{s_j = \pm 1} \prod_{j=1,2,\dots,N} \exp \left\{ \frac{h}{2T} s_j + \frac{J}{T} s_j s_{j+1} + \frac{h}{2T} s_{j+1} + C \right\}. \quad (4.105)$$

Let us group each two adjacent exponents to recast this expression as a product over only *even* numbers j ,

$$Z = \sum_{s_j = \pm 1} \prod_{j=2,4,\dots,N} \exp \left\{ \frac{h}{2T} s_{j-1} + s_j \left[\frac{J}{T} (s_{j-1} + s_{j+1}) + \frac{h}{T} \right] + \frac{h}{2T} s_{j+1} + 2C \right\}, \quad (4.106)$$

and carry out the summation over two possible states of the internal spins s_j explicitly:

$$\begin{aligned} Z &= \sum_{\substack{s_j = \pm 1 \\ (\text{for odd } j)}} \prod_{j=2,4,\dots,N} \left[\exp \left\{ \frac{h}{2T} s_{j-1} + \frac{J}{T} (s_{j-1} + s_{j+1}) + \frac{h}{T} + \frac{h}{2T} s_{j+1} + 2C \right\} \right. \\ &\quad \left. + \exp \left\{ \frac{h}{2T} s_{j-1} - \frac{J}{T} (s_{j-1} + s_{j+1}) - \frac{h}{T} + \frac{h}{2T} s_{j+1} + 2C \right\} \right] \\ &= \sum_{\substack{s_j = \pm 1 \\ (\text{for odd } j)}} \prod_{j=2,4,\dots,N} 2 \cosh \left\{ \frac{J}{T} (s_{j-1} + s_{j+1}) + \frac{h}{T} \right\} \exp \left\{ \frac{h}{2T} (s_{j-1} + s_{j+1}) + 2C \right\}. \end{aligned} \quad (4.107)$$

Now let us require this statistical sum (and hence all statistical properties of the system of 2-spin blocks) to be identical to that of the Ising system of $N/2$ spins, numbered by odd j :

$$Z' = \sum_{\substack{s_j = \pm 1 \\ (\text{for odd } j)}} \prod_{j=2,4,\dots,N} \exp \left\{ \frac{J'}{T} s_{j-1} s_{j+1} + \frac{h'}{T} s_{j+1} + C' \right\}, \quad (4.108)$$

with some different parameters h' , J' , and C' , for all 4 possible values of $s_{j-1} = \pm 1$ and $s_{j+1} = \pm 1$. Since the right-hand part of Eq. (107) depends only on the sum $(s_{j-1} + s_{j+1})$, this requirement yields only 3 (rather than 4) independent equations for finding h' , J' , and C' . Of them, equations for h' and J' depend only on h and J (but not on C),⁵¹ and may be presented in an especially simple form,

⁵⁰ Developed first in the quantum field theory in the 1950s, it was adapted to statistics by L. Kadanoff in 1966, with a spectacular solution of the so-called Kubo problem by K. Wilson in 1972, later awarded by a Nobel Prize.

⁵¹ This might be expected, because physically C is just a certain constant addition to system's energy. However, the introduction of that constant is mathematically necessary, because Eqs. (107) and (108) may be reconciled only if $C' \neq C$.

RG
equations
for 1D Ising
model

$$x' = \frac{x(1+y)^2}{(x+y)(1+xy)}, \quad y' = \frac{y(x+y)}{1+xy}, \quad (4.109)$$

using notation

$$x \equiv \exp\left\{-4\frac{J}{T}\right\}, \quad y \equiv \exp\left\{-2\frac{h}{T}\right\}. \quad (4.110)$$

Now the grouping procedure may be repeated, with the same result (109)-(110). Hence these equations may be considered as recurrence relations describing repeated doubling of the spin block size. Figure 15 shows (schematically) the *trajectories* of this dynamic system on the phase plane $[x, y]$. (A trajectory is defined by the following property: for each of its points $\{x, y\}$, the point $\{x', y'\}$ defined by the “mapping” Eq. (109) is also on the same trajectory.) For ferromagnetic coupling ($J > 0$) and $h > 0$, we may limit the analysis to the unit square $0 \leq x, y \leq 1$. If this *flow diagram* had a stable fixed point with $x' = x = x_\infty \neq 0$ (i.e. $T/J < \infty$) and $y' = y = 1$ (i.e. $h = 0$), then the first of Eqs. (110) would immediately give us the critical temperature of the phase transition in the field-free system:

$$T_c = \frac{4J}{\ln(1/x_\infty)}. \quad (4.111)$$

However, Fig. 15 shows that the only fixed point of the 1D system is $x = y = 0$, which (at finite coupling J) should be interpreted as $T_c = 0$. This is of course in agreement with the exact result of the transfer-matrix analysis, but does not give any additional information.

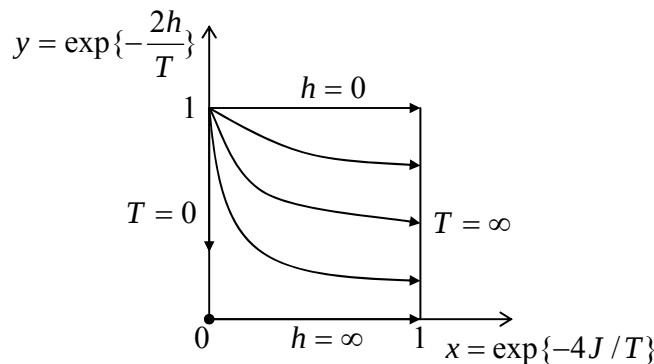


Fig. 4.15. The RG flow diagram of the 1D Ising system (schematically).

Unfortunately, for higher dimensionalities the renormalization-group approach rapidly becomes rather cumbersome, and requires certain approximations, whose accuracy cannot be easily controlled. For 2D Ising system, such approximations lead to the prediction $T_c/J \approx 2.55$, i.e. to a substantial difference from the exact (Onsager's) result.

4.6. Exercise problems

4.1. Compare the third virial coefficient $C(T)$ for the hardball model of particle interactions, that follows from the van der Waals equation, with the exact result (whose calculation was the subject of Problem 3.18).

4.2. Calculate the entropy and the internal energy of the van der Waals gas, and discuss the results.

4.3. Use two different approaches to calculate $(\partial E/\partial V)_T$ for the van der Waals gas, and the change of temperature of such a gas, with temperature-independent C_V , at its fast expansion into free space.

4.4.* Derive as many analytical results as you can for temperature dependence of the phase-equilibrium pressure $P_0(T)$ and the latent heat $\Lambda(T)$ within the van der Waals model. In particular, explore the low-temperature limit ($T \ll T_c$), and the close vicinity of the critical point T_c .

4.5.* Calculate the critical values P_c , V_c , and T_c for the so-called *Redlich-Kwong model* of the real gas, with the following phenomenological equation of state:⁵²

$$P + \frac{a}{V(V + Nb)T^{1/2}} = \frac{NT}{V - Nb}.$$

Hint: Be prepared to solve a cubic equation with particular (numerical) coefficients.

4.6. Use the Clapeyron-Clausius formula (4.17) to calculate the latent heat Λ of the Bose-Einstein condensate, and compare the result with that obtained in Problem 3.18.

4.7. In the simplest model of the liquid-gas equilibrium,⁵³ temperature and pressure do not affect molecule's condensation energy Δ . Calculate the concentration and pressure of the gas over liquid's surface, assuming that its molecules are classical, non-interacting particles.

4.8. Assuming the hardball model, with volume V_0 per molecule, for the liquid phase, but still treating the gaseous phase an ideal gas, describe how do the results of the previous problem change if the liquid phase is in the form of spherical drops of radius $R \gg V_0^{1/3}$. Briefly discuss the implications of the result for water cloud formation.

4.9. A classical ideal gas of $N \gg 1$ particles is placed into a container of volume V and wall surface area A . The particles may condense on container walls, loosing potential energy Δ per particle, and forming an ideal 2D gas. Calculate the equilibrium number of condensed particles and gas pressure, and discuss their temperature dependences.

4.10. The inner surfaces of the walls of a closed container of volume V , filled with $N \gg 1$ indistinguishable particles, have $N_S \gg 1$ similar traps (small potential wells). Each trap can hold only one particle, at energy $-\Delta < 0$. Assuming that the gas is ideal and classical, derive the equation for the chemical potential μ of the system in equilibrium, and use it to calculate the potential and the gas pressure in the limits of small and large values of the ratio N/N_S .

⁵² This equation of state, suggested in 1948, describes most real gases better than not only the original van der Waals model, but also its later 2-parameter alternatives, such as the *Berthelot*, *modified-Berthelot*, and *Dieterici models*, though approximations with more fitting parameters (such as the *Soave-Redlich-Kwong model*) work even better.

⁵³ For real liquids, the model is reasonable only within certain parameter ranges.

4.11. Superconductivity may be suppressed by a sufficiently strong magnetic field. In the simplest case of a bulk, long cylindrical sample of the type-I superconductor, placed into an external magnetic field $\mathcal{B}_{\text{ext}}$ parallel to its surface, this suppression takes a form of a simultaneous transition of the whole sample from the superconducting to the “normal” (non-superconducting) state at certain critical magnitude $\mathcal{B}_c(T)$. The critical field gradually decreases with temperature from the maximum value $\mathcal{B}_c(0)$ at $T \rightarrow 0$ to zero at the critical temperature T_c . Assuming that the function $\mathcal{B}_c(T)$ is known, calculate the latent heat of transition as a function of temperature, and find its values at $T \rightarrow 0$ and $T = T_c$.

Hint: In this context, “bulk” means a sample much larger than the intrinsic length scales of the superconductor (such as the London penetration depth δ_L and the coherence length ξ).⁵⁴ For such bulk samples, magnetic properties of the superconducting state may be well described just as a perfect diamagnetism, with zero magnetic permeability μ .

4.12. In some textbooks, the discussion of thermodynamics of superconductivity is started with displaying, as self-evident, the following formula:

$$F_n(T) - F_s(T) = \frac{B_c^2(T)}{2\mu_0} V,$$

where F_s and F_n are the free energy values in the superconducting and non-superconducting (“normal”) phases, and $\mathcal{B}_c(T)$ is the critical value of field. Is this formula correct, and if not, what modification is necessary to make it valid? Assume that all conditions of the simultaneous field-induced phase transition in the whole sample, spelled out in the previous problem, are satisfied.

4.13. In Sec. 4, we have discussed Weiss’ molecular-field approach to the Ising model, in which the lattice average $\langle s_j \rangle$ plays the role of the order parameter η . Use the results of that analysis to find coefficients a and b in the corresponding Landau expansion (46) of the free energy. List the values of critical exponents α and β , defined by Eqs. (26) and (28), within this approach.

4.14. Calculate the average order parameter and the low-field susceptibility χ of a ring of three Ising-type “spins” ($s_j = \pm 1$), with similar ferromagnetic coupling J between all sites, in thermal equilibrium. From the result, can you predict the low-temperature behavior of χ in an N -spin ring?

4.15. Use Eq. (88) to calculate the average energy, free energy, entropy and heat capacity (all per lattice site), as functions of temperature T and field h , for the 1D Ising model. Sketch the temperature dependence of the heat capacity for various values of ratio h/J , and give a physical interpretation of the result.

4.16. Use the molecular-field theory to calculate the critical temperature and low-field susceptibility of a d -dimensional cubic lattice of spins described by the so-called *classical Heisenberg model*.⁵⁵

⁵⁴A brief discussion of these parameters, as well as of the difference between the type-I and type-II superconductivity, may be found in EM Secs. 6.3-6.4.

⁵⁵This model is formally similar to the genuine (quantum) Heisenberg model – see Eq. (21).

$$E_m = -J \sum_{\{jj'\}} \mathbf{s}_j \cdot \mathbf{s}_{j'} - \sum_j \mathbf{h} \cdot \mathbf{s}_j .$$

Here, in contrast to the (otherwise, very similar) Ising model (23), the spin of each site is modeled by a classical 3D vector $\mathbf{s}_j = \{s_{xj}, s_{yj}, s_{zj}\}$ of unit length: $s_j^2 = 1$.

Chapter 5. Fluctuations

This chapter discusses fluctuations of statistical variables, mostly at thermodynamic equilibrium. In particular, I will describe the intimate connection between fluctuations and dissipation (damping) in a dynamic system weakly coupled to a multi-particle environment, which culminates in the Einstein relation between the diffusion coefficient and mobility, the Nyquist formula, and their quantum-mechanical generalization - the fluctuation-dissipation theorem. An alternative approach to the same problem, based on the Smoluchowski and Fokker-Planck equations, is also discussed in brief.

5.1. Characterization of fluctuations

In the beginning of Chapter 2, we have discussed the notion of averaging, $\langle f \rangle$, of a variable f over a statistical ensemble – see Eqs. (2.7) and (2.10). Now, the variable's *fluctuation* may be defined simply as its deviation from the average:

Fluctuation

$$\tilde{f} \equiv f - \langle f \rangle; \quad (5.1)$$

this deviation is, evidently, also a random variable. The most important property of any fluctuation is that its average (over the same statistical ensemble) equals zero:

$$\langle \tilde{f} \rangle = \langle f - \langle f \rangle \rangle = \langle f \rangle - \langle \langle f \rangle \rangle = \langle f \rangle - \langle f \rangle = 0. \quad (5.2)$$

As a result, such average cannot characterize fluctuations' *intensity*, whose simplest characteristic is the *variance* (also called “dispersion”):

Variance:
definition

$$\langle \tilde{f}^2 \rangle = \langle (f - \langle f \rangle)^2 \rangle. \quad (5.3)$$

The following simple property of the variance is frequently convenient for its calculation:

$$\langle \tilde{f}^2 \rangle = \langle (f - \langle f \rangle)^2 \rangle = \langle f^2 - 2f\langle f \rangle + \langle f \rangle^2 \rangle = \langle f^2 \rangle - 2\langle f \rangle^2 + \langle f \rangle^2, \quad (5.4a)$$

so that, finally:

Variance
via
averages

$$\langle \tilde{f}^2 \rangle = \langle f^2 \rangle - \langle f \rangle^2. \quad (5.4b)$$

As the simplest example of its application, consider a variable which can take only two values, ± 1 , with equal probabilities $W_j = 1/2$. For such a variable,

$$\langle f \rangle = \sum_j W_j f_j = \frac{1}{2}(+1) + \frac{1}{2}(-1) = 0, \quad \text{but} \quad \langle f^2 \rangle = \sum_j W_j f_j^2 = \frac{1}{2}(+1)^2 + \frac{1}{2}(-1)^2 = 1, \quad (5.5)$$

so that $\langle \tilde{f}^2 \rangle = \langle f^2 \rangle - \langle f \rangle^2 = 1.$

The square root of variance,

R.m.s.
fluctuation

$$\delta f \equiv \langle \tilde{f}^2 \rangle^{1/2} \quad (5.6)$$

is called the *root-mean-square (r.m.s.) fluctuation*. An advantage of this measure is that it has the same dimensionality as the variable itself, so that ratio $\delta f / \langle f \rangle$ is dimensionless, and may be used to characterize the *relative intensity* of fluctuations. In particular, as has been mentioned in Chapter 1, all results of thermodynamics are valid only if the fluctuations of thermodynamic variables (internal energy E , entropy S , etc.) are relatively small.¹ Let us make the simplest estimate of the relative intensity of fluctuations by considering a system of N independent, similar particles, and an extensive variable

$$\mathcal{F} \equiv \sum_{j=1}^N f_j . \quad (5.7)$$

where f_j depends on the state of just one (j^{th}) particle. The statistical average of $\mathcal{F}$ is evidently

$$\langle \mathcal{F} \rangle = \sum_{j=1}^N \langle f_j \rangle = N \langle f \rangle, \quad (5.8)$$

while the variance is

$$\langle \tilde{\mathcal{F}}^2 \rangle = \left\langle \sum_{j=1}^N \tilde{f}_j \sum_{j'=1}^N \tilde{f}_{j'} \right\rangle = \left\langle \sum_{j,j'=1}^N \tilde{f}_j \tilde{f}_{j'} \right\rangle = \sum_{j,j'=1}^N \langle \tilde{f}_j \tilde{f}_{j'} \rangle. \quad (5.9)$$

Now we may use the fact that for two independent variables

$$\langle \tilde{f}_j \tilde{f}_{j'} \rangle = 0; \quad (5.10)$$

actually, this equation may be considered as the mathematical definition of the independence. Hence, in the sum (9), only the terms with $j' = j$ survive, and

$$\langle \tilde{\mathcal{F}}^2 \rangle = \sum_{j,j'=1}^N \langle \tilde{f}_j^2 \rangle \delta_{j,j'} = N \langle \tilde{f}^2 \rangle. \quad (5.11)$$

Comparing Eqs. (8) and (11), we see that the relative intensity of fluctuations of variable $\mathcal{F}$

$$\boxed{\frac{\delta \mathcal{F}}{\langle \mathcal{F} \rangle} = \frac{1}{N^{1/2}} \frac{\delta f}{\langle f \rangle}}, \quad (5.12) \quad \text{Relative fluctuation estimate}$$

tends to zero as the system size grows ($N \rightarrow \infty$). It is this fact that justifies the thermodynamic approach to typical physical systems, with the number N of particles of the order of the Avogadro number $N_A \approx 10^{24}$. Nevertheless, in many situations even small fluctuations of thermodynamic variables are important, and in this chapter we will calculate their basic properties, starting from the variance.

It will be pleasant for the reader to notice that for some simple (but important) cases, such calculation has already been done in our course. For example, for any generalized coordinate q_j and generalized momentum p_j that give quadratic contributions to system's Hamiltonian (2.46), we have derived the equipartition theorem (2.48), valid in the classical limit. Since the average values of these

¹ Let me remind the reader that up to this point, the averaging signs $\langle \dots \rangle$ were dropped in most formulas, for the sake of notation simplicity. In this chapter I have to restore these signs to avoid confusion. The only exception will be temperature whose average, following (bad :-)) tradition, will be still call T everywhere besides the last part of Sec. 3 where temperature fluctuations are discussed explicitly.

variables, in the thermodynamic equilibrium, equal zero, Eq. (6) immediately yields their r.m.s. fluctuations:

$$\delta p_j = (mT)^{1/2}, \quad \delta q_j = \left(\frac{T}{m\omega^2} \right)^{1/2}. \quad (5.13)$$

The generalization of these classical relations to the quantum-mechanical case ($T \sim \hbar\omega$) for a 1D harmonic oscillator is provided by Eqs. (2.78) and (2.81):

$$\delta p_j = \left[\frac{\hbar m \omega}{2} \coth \frac{\hbar \omega}{2T} \right]^{1/2}, \quad \delta q_j = \left[\frac{\hbar}{2m \omega} \coth \frac{\hbar \omega}{2T} \right]^{1/2}. \quad (5.14)$$

However, the intensity of fluctuations in other systems requires special calculations. Moreover, only a few cases allow for general, model-independent results. Let us review some of them.

5.2. Energy and the number of particles

First of all, note that fluctuations of macroscopic variables depend on particular conditions.² For example, in a mechanically- and thermally-insulated system, e.g., a member of a microcanonical ensemble, there are no fluctuations of internal energy: $\delta E = 0$.

However, if a system is in a thermal contact with environment, for example is a member of a canonical ensemble (Fig. 2.6), the Gibbs distribution (2.58)-(2.59) is valid. We already know that application of this distribution to energy itself,

$$\langle E \rangle = \sum_m W_m E_m, \quad W_m = \frac{1}{Z} \exp \left\{ -\frac{E_m}{T} \right\}, \quad Z = \sum_m \exp \left\{ -\frac{E_m}{T} \right\}, \quad (5.15)$$

yields Eq. (2.61b), which may be rewritten in the form

$$\langle E \rangle = \frac{1}{Z} \frac{\partial Z}{\partial (-\beta)}, \quad \text{with } \beta \equiv \frac{1}{T}, \quad (5.16)$$

more convenient for our current purposes. Now let us carry out a similar calculation for variable E^2 :

$$\langle E^2 \rangle = \sum_m W_m E_m^2 = \frac{1}{Z} \sum_m E_m^2 \exp \{ -\beta E_m \}. \quad (5.17)$$

It is straightforward to check, by double differentiation, that this expression may be rewritten as

$$\langle E^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial (-\beta)^2} \sum_m \exp \{ -\beta E_m \} = \frac{1}{Z} \frac{\partial^2 Z}{\partial (-\beta)^2}. \quad (5.18)$$

Now it is straightforward to use Eq. (4) to calculate the energy fluctuation variance:

$$\langle \tilde{E}^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial (-\beta)^2} - \frac{1}{Z^2} \left(\frac{\partial Z}{\partial (-\beta)} \right)^2 = \frac{\partial}{\partial (-\beta)} \left(\frac{1}{Z} \frac{\partial Z}{\partial (-\beta)} \right) = \frac{\partial \langle E \rangle}{\partial (-\beta)}. \quad (5.19)$$

² Unfortunately, even in some popular textbooks, a few formulas pertaining to fluctuations are either incorrect, or given without specifying the conditions of their applicability, so that reader's caution is advised.

Since Eq. (15) is valid only if system's volume V is fixed, it is customary to rewrite this extremely simple and important result as follows:

$$\langle \tilde{E}^2 \rangle = \frac{\partial \langle E \rangle}{\partial(-1/T)} = T^2 \left(\frac{\partial \langle E \rangle}{\partial T} \right)_V = C_V T^2. \quad (5.20) \quad \text{Fluctuations of } E$$

This is a remarkably simple, fundamental result. As a sanity check, for a system of N similar, independent particles, $\langle E \rangle$ and hence C_V and are proportional to N , so that $\delta E \propto N^{1/2}$ and $\delta E / \langle E \rangle \propto N^{-1/2}$, in agreement with Eq. (12). Let me emphasize that the classically-looking Eq. (20) is based on the general Gibbs distribution, and hence is valid for any system – either classical or quantum.

We will discuss the corollaries of this result in the next section, and now let me carry out a very similar calculation for a system whose number N of particles in a system is not fixed, because they may go to, and come from the environment at will. If the chemical potential μ of the environment and its temperature T are fixed, we are dealing with the grand canonical ensemble (Fig. 2.13), and may use the grand canonical distribution (2.106)-(2.107):

$$W_{m,N} = \frac{1}{Z_G} \exp \left\{ \frac{\mu N - E_{m,N}}{T} \right\}, \quad Z_G = \sum_{N,m} \exp \left\{ \frac{\mu N - E_{m,N}}{T} \right\}. \quad (5.21)$$

Acting exactly as we did above for energy, we get

$$\langle N \rangle = \frac{1}{Z_G} \sum_{m,N} N \exp \left\{ \frac{\mu N - E_{m,N}}{T} \right\} = \frac{T}{Z_G} \frac{\partial Z_G}{\partial \mu}, \quad (5.22)$$

$$\langle N^2 \rangle = \frac{1}{Z_G} \sum_{m,N} N^2 \exp \left\{ \frac{\mu N - E_{m,N}}{T} \right\} = \frac{T^2}{Z_G} \frac{\partial^2 Z_G}{\partial \mu^2}, \quad (5.23)$$

so that the particle number variance is

$$\langle \tilde{N}^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 = \frac{T^2}{Z_G} \frac{\partial Z_G}{\partial \mu} - \frac{T^2}{Z_G^2} \left(\frac{\partial Z_G}{\partial \mu} \right)^2 = T \frac{\partial}{\partial \mu} \left(\frac{T}{Z_G} \frac{\partial Z_G}{\partial \mu} \right) = T \frac{\partial \langle N \rangle}{\partial \mu}, \quad (5.24) \quad \text{Fluctuations of } N$$

in the full analogy with Eq. (19).

For example, for the ideal classical gas we had Eq. (3.32). As was already emphasized in Sec. 3.2, though that result has been obtained from the canonical ensemble in that the number of particles N is fixed, at $N \gg 1$ the fluctuations of N in the grand canonical ensemble should be relatively small, so that the same relation should be valid for *average* $\langle N \rangle$ in that ensemble. Solving that relation for $\langle N \rangle$, we get

$$\langle N \rangle = \text{const} \times \exp \left\{ \frac{\mu}{T} \right\}, \quad (5.25)$$

where “const” means a factor that is constant at the differentiation of $\langle N \rangle$ over μ , required by Eq. (24). Performing the differentiation and then using Eq. (25) again,

$$\frac{\partial \langle N \rangle}{\partial \mu} = \text{const} \times \frac{1}{T} \exp \left\{ \frac{\mu}{T} \right\} = \frac{\langle N \rangle}{T}, \quad (5.26)$$

we get from Eq. (24) a surprisingly simple result:

Fluctuations
of N in
classical gas

$$\langle \tilde{N}^2 \rangle = \langle N \rangle, \quad \text{i.e. } \delta N = \langle N \rangle^{1/2} \quad (5.27)$$

This relation is so simple and important that I will now show how it may be derived in a different way, in order to prove that this result is valid for systems with an arbitrary (say, small) N , and also get more detailed information about the statistics of fluctuations of that number. Let us consider an ideal classical gas of N_0 particles in a volume V_0 , and calculate the probability W_N to have exactly $N \leq N_0$ of these particles in a part $V \leq V_0$ of this volume – see Fig. 1.

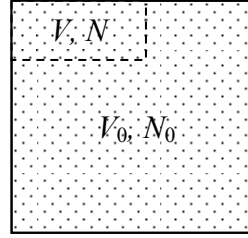


Fig. 5.1. Deriving the binomial and Poissonian distributions.

For one particle such probability is of course $W = V/V_0 \leq 1$, while the probability of one particle being in the remaining part of the volume is $W' = 1 - W = 1 - V/V_0$. If all particles were distinguishable, the probability of having $N \leq N_0$ *specific* particles in volume V , and $(N - N_0)$ *specific* particles in volume $(V - V_0)$, would be $W^N W'^{(N_0 - N)}$. However, if we do not distinguish the particles, we should multiply the probability by the number of possible particle combinations keeping numbers N and N_0 constant, i.e. by the binomial coefficient $N_0! / N!(N_0 - N)!$.³ As the result, the required probability is

Binomial
distribution

$$W_N = W^N W'^{(N_0 - N)} \frac{N_0!}{N!(N_0 - N)!} = \left(\frac{\langle N \rangle}{N_0} \right)^N \left(1 - \frac{\langle N \rangle}{N_0} \right)^{N_0 - N} \frac{N_0!}{N!(N_0 - N)!}, \quad (5.28)$$

where in the second instance I have used the evident expression $\langle N \rangle = W N_0 = (V/V_0) N_0$ for the average number of particles in volume V . Relation (28) is the so-called *binomial probability distribution*, valid for *any* $\langle N \rangle$ and N_0 .

If we are interested in keeping $\langle N \rangle$ arbitrary, but do not care how large the additional volume $(V_0 - V)$ is, we can simplify the binomial distribution by assuming that the external part, and hence N_0 , are very large:

$$N_0 \gg N, \quad (5.29)$$

where N means all values of interest, including $\langle N \rangle$. In this limit we can neglect N in comparison with N_0 in the second exponent of Eq. (28), and also approximate the fraction $N_0! / (N_0 - N)!$, i.e. the product of N terms, $(N_0 - N + 1)(N_0 - N + 2) \dots (N_0 - 1)N_0$, as just N_0^N . As a result, we get

$$W_N \approx \left(\frac{\langle N \rangle}{N_0} \right)^N \left(1 - \frac{\langle N \rangle}{N_0} \right)^{N_0} \frac{N_0^N}{N!} = \frac{\langle N \rangle^N}{N!} \left(1 - \frac{\langle N \rangle}{N_0} \right)^{N_0} = \frac{\langle N \rangle^N}{N!} \left[(1 - W)^{\frac{1}{W}} \right]^{\langle N \rangle}. \quad (5.30)$$

³ See, e.g., MA Eq. (2.2).

In the limit (29), $W \rightarrow 0$, and factor inside the square brackets tends to $1/e$, the reciprocal of the natural logarithm base.⁴ Thus, we finally get an expression independent of N_0 :

$$W_N = \frac{\langle N \rangle^N}{N!} e^{-\langle N \rangle}.$$

(5.31)

Poisson
distribution

This is the much celebrated *Poisson distribution*, which describes a very broad family of random phenomena. Figure 2 shows this distribution for several values of $\langle N \rangle$ - which, in contrast to N , are not necessarily integer.

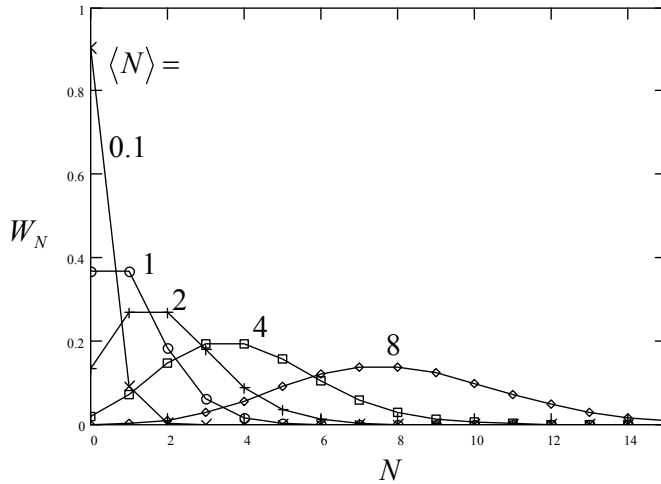


Fig. 5.2. The Poisson distribution for several values of $\langle N \rangle$. In contrast to that average, argument N may take only integer values, so that lines are only guides for the eye.

At very small $\langle N \rangle$, function $W_N(N)$ distribution is close to an exponential one, $W_N \approx W^N \propto \langle N \rangle^N$, while in the opposite limit, $\langle N \rangle \gg 1$, it rapidly approaches the *Gaussian* (alternatively called “normal”) distribution

$$W_N = \frac{1}{(2\pi)^{1/2} \delta N} \exp\left\{-\frac{(N - \langle N \rangle)^2}{2(\delta N)^2}\right\}, \quad \text{with } \delta N = \langle N \rangle^{1/2}.$$

(5.32)

Gaussian
distribution

(Note that the Gaussian distribution is also valid if both N and N_0 are large, regardless of relation (29) between them - see Fig. 3.)

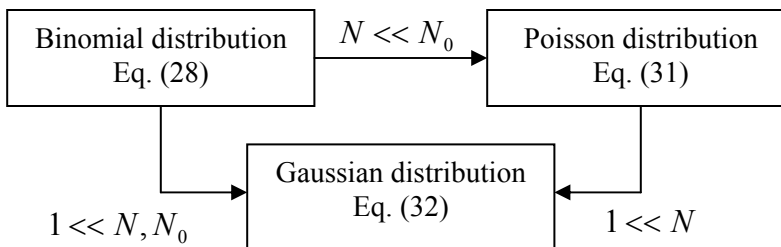


Fig. 5.3. Hierarchy of three major probability distributions.

⁴ Indeed, this is the most popular definition of this major mathematical constant – see, e.g., MA Eq. (1.2a) with n replaced with $-1/W$.

The key property of the Poisson (and hence of the Gaussian) distribution is that it has the same variance as given by Eq. (27):

$$\langle \tilde{N}^2 \rangle \equiv \langle (N - \langle N \rangle)^2 \rangle = \langle N \rangle. \quad (5.33)$$

(This is not true for the general binomial distribution.) For our current purposes, this means that for the ideal classical gas, Eq. (27) is valid for *any* number of particles.

5.3. Volume and temperature

What are the r.m.s. fluctuations of other thermodynamic variables – like V , T , etc.? Again, the answer depends on conditions. For example, if the volume V occupied by a gas is externally fixed (say, by rigid walls), it evidently does not fluctuate at all: $\delta V = 0$. On the other hand, the volume may fluctuate in the situation when average pressure is fixed – see, e.g., Fig. 1.5. A formal calculation of these fluctuations, using the approach applied in the last section, is hampered by the fact that it is physically impracticable to fix its conjugate variable, P , i.e. suppress its fluctuations. For example, the force $\mathcal{F}(t)$ exerted by an ideal classical gas on vessel's wall (whose measure the pressure is) is the result of individual, independent hits of the wall by particles (Fig. 4), with time scale $\tau_c \sim r_B/(T/m)^{1/2} \sim 10^{-16}$ s, so that its frequency spectrum extends to very high frequencies, virtually impossible to control.

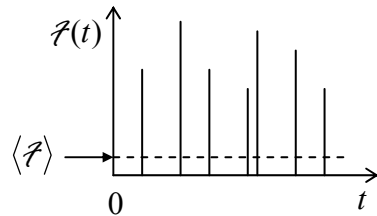


Fig. 5.4. Force exerted by gas particles on container's wall, as a function of time (schematically).

However, we can use the following trick, very typical for the theory of fluctuations. It is almost evident that r.m.s. fluctuations of volume are independent of the shape of the container. Let us consider the particular situation similar to that shown in Fig. 1.5, with the container of a cylindrical shape, with the base area A .⁵ Then the coordinate of the piston is just $q = V/A$, while the average force exerted by the gas on the cylinder is $\mathcal{F} = PA$ – see Fig. 5. Now if the piston is sufficiently massive, its free oscillation frequency ω near the equilibrium position is small enough to satisfy the following three conditions.

First, besides balancing the average force $\langle \mathcal{F} \rangle$, and thus sustaining average pressure $\langle P \rangle = \langle \mathcal{F} \rangle / A$ of the gas, the interaction between the heavy piston and light molecules of the gas is weak because of a relatively short duration of the wall hits (Fig. 4). Because of that, the full energy of the system may be presented as a sum of those of the gas and the piston, with a quadratic contribution to piston's potential energy from small deviations of equilibrium:

$$U_p = \frac{\kappa}{2} \tilde{q}^2, \quad \tilde{q} \equiv q - \langle q \rangle = \frac{\tilde{V}}{A}, \quad (5.34)$$

⁵ As a reminder, in geometry the term “cylinder” does not necessarily means the “circular cylinder”; the shape of base A may be arbitrary; it just should not change with height.

where κ is the effective spring constant arising from gas' compressibility.

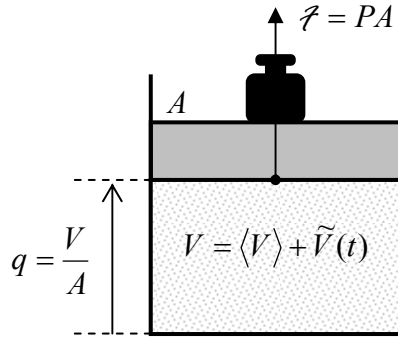


Fig. 5.5. Deriving Eq. (37).

Second, at $\omega \rightarrow 0$, that spring constant may be calculated just as for constant variations of volume, with the gas remaining in quasi-equilibrium at all times:

$$\kappa = -\frac{\partial \langle F \rangle}{\partial q} = A^2 \left(-\frac{\partial \langle P \rangle}{\partial \langle V \rangle} \right). \quad (5.35)$$

This partial derivative⁶ should be taken at whatever the given thermal conditions are, e.g., with $S = \text{const}$ for adiabatic conditions (i.e., thermally insulated gas), or with $T = \text{const}$ for isothermic conditions (gas in a good thermal contact with a heat bath), etc. With that constant denoted as X , Eqs. (34)-(35) give

$$U_P = \frac{1}{2} \left(-A^2 \frac{\partial \langle P \rangle}{\partial \langle V \rangle} \right)_X \left(\frac{\tilde{V}}{A} \right)^2 = \frac{1}{2} \left(-\frac{\partial \langle P \rangle}{\partial \langle V \rangle} \right)_X \tilde{V}^2. \quad (5.36)$$

Finally, making ω sufficiently small (namely, $\hbar\omega \ll T$) by a sufficiently large piston mass, we can apply, to the piston's fluctuations, the classical equipartition theorem: $\langle U_P \rangle = T/2$, giving

$$\boxed{\langle \tilde{V}^2 \rangle_X = T \left(-\frac{\partial \langle V \rangle}{\partial \langle P \rangle} \right)_X} \quad (5.37a) \quad \text{Fluctuations of volume}$$

Since this result is valid for any A and ω , it should not depend on system's geometry and piston mass, provided that it is large in comparison with the effective mass of a single system component (say, a gas molecule) – the condition that is naturally fulfilled in most experiments.⁷ For the particular case of fluctuations at constant temperature ($X = T$), we may use the second of Eqs. (1.39) to rewrite Eq. (37a) as

⁶ As already was discussed in Sec. 4.1 in the context of the van der Waals equation, for mechanical stability of a gas (or liquid), derivative $\partial P / \partial V$ has to be negative, so that κ is positive.

⁷ One may meet statements that a similar formula,

$$\langle \tilde{P}^2 \rangle = T \left(-\frac{\partial \langle P \rangle}{\partial \langle V \rangle} \right)_X, \quad \text{WRONG!}$$

is valid for pressure fluctuations. However, such statement does not take into account a different physical nature of pressure (Fig. 4), with its very broad frequency spectrum. This issue will be discussed later in this chapter.

$$\langle \tilde{V}^2 \rangle_T = -T \left(\frac{\partial^2 G}{\partial \langle P \rangle^2} \right)_T. \quad (5.37b)$$

In the specific case of an ideal classical gas of N particles, with the equation of state $\langle V \rangle = NT/\langle P \rangle$, it is easier to use directly Eq. (37a), with $X = T$, to get

$$\langle \tilde{V}^2 \rangle_T = -T \left(-\frac{NT}{\langle P \rangle^2} \right) \equiv \frac{\langle V \rangle^2}{N}, \quad \text{i.e. } \frac{\delta V_T}{\langle V \rangle} = \frac{1}{N^{1/2}}, \quad (5.38)$$

in agreement with the trend given by Eq. (12).

Now let us proceed to fluctuations of temperature, for simplicity focusing on the case $V = \text{const.}$ Let us again assume that the system we are considering is weakly coupled to a heat bath of temperature T_0 , in the sense that the time τ of temperature equilibration between the two is much larger than the internal temperature relaxation (*thermalization*) time. Then we may assume that T changes in the whole system virtually simultaneously, and consider it a function of time alone:

$$T = \langle T \rangle + \tilde{T}(t). \quad (5.39)$$

Moreover, due to the (relatively) large τ , we may use the stationary relation between small fluctuations of temperature and the internal energy of the system:

$$\tilde{T}(t) = \frac{\tilde{E}(t)}{C_V}, \quad \text{so that } \delta T = \frac{\delta E}{C_V}. \quad (5.40)$$

With those assumptions, Eq. (20) immediately yields the famous expression for the so-called *thermodynamic fluctuations of temperature*:

$$\delta T = \frac{\delta E}{C_V} = \frac{\langle T \rangle}{C_V^{1/2}}. \quad (5.41)$$

The most straightforward application of this result is to analysis of so-called *bolometers* - broadband detectors of electromagnetic radiation in microwave and infrared frequency bands. In such a detector (Fig. 6), the incoming radiation is focused on a small sensor (e.g., either a small piece of a Ge crystal, or a superconductor thin film at temperature $T \approx T_c$, etc.) that is well isolated thermally from the environment.

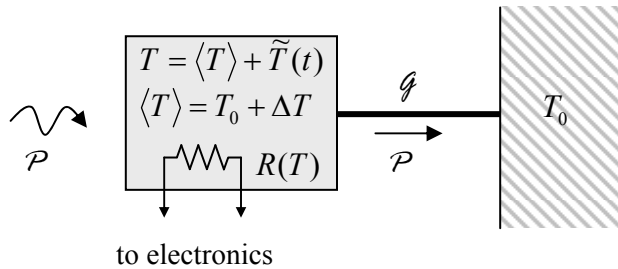


Fig. 5.6. Conceptual scheme of a bolometer.

As a result, the absorption of even small radiation power $\mathcal{P}$ leads to a noticeable change ΔT of sensor's average temperature $\langle T \rangle$ and hence of its electric resistance R , which is probed up by low-noise

external electronics.⁸ If power does not change in time too fast, ΔT is a certain function of $\mathcal{P}$, turning into 0 at $\mathcal{P}=0$. Hence, if ΔT is much lower than the environment temperature T_0 , we may keep only the main, linear term in its Taylor expansion in $\mathcal{P}$.

$$\Delta T \equiv \langle T \rangle - T_0 = \frac{\mathcal{P}}{\mathcal{G}}, \quad (5.42)$$

where coefficient $\mathcal{G} \equiv \partial \mathcal{P} / \partial T$ is called the *thermal conductance* of the unavoidable thermal coupling between the sensor and the heat bath – see Fig. 6. The power may be detected if the electric signal from the sensor, which results from change ΔT , is not drowned in spontaneous fluctuations. In practical systems, these fluctuations are contributed by several sources including electronic amplifiers, sensor, etc. However, in modern systems these “technical” contributions to noise are successfully suppressed, and the dominating noise source are the fundamental fluctuations of sensor temperature, described by Eq. (41). In this case the so-called *noise-equivalent power* (“NEP”), defined as the level of $\mathcal{P}$ that produces signal equal to r.m.s. value of noise, may be calculated by equating Eqs. (41) (with $\langle T \rangle \approx T_0$) and (42):

$$\text{NEP} = \frac{T_0 \mathcal{G}}{C_V^{1/2}}. \quad (5.43)$$

This expression shows that in order to decrease *NEP*, i.e. improve the device sensitivity, both the environment temperature T_0 and thermal conductance $\mathcal{G}$ should be reduced. In modern receivers of radiation, their typical values (in SI units) are of the order of 0.1 K and 10^{-10} W/K, respectively.

On the other hand, Eq. (43) implies that in order to increase bolometer sensitivity, i.e. reduce NEP, the C_V of the sensor, and hence its mass, should be *increased*. This conclusion is valid only to a certain extent, because due to technical reasons (parameter drift and the so-called *1/f noise* of the sensor and external electronics), incoming power has to be modulated with as high frequency ω as possible (in most cases, the cyclic frequency $\nu = \omega/2\pi$ of the modulation is between 10 to 1,000 Hz), so that the electrical signal may be picked up from the sensor at that frequency. As a result, C_V may be increased only until the thermal constant of the sensor,

$$\tau = \frac{C_V}{\mathcal{G}}, \quad (5.44)$$

becomes close to $1/\omega$, because at $\omega\tau \gg 1$ the useful signal drops faster than noise. As a result, the lowest (i.e. the best) value of NEP,

$$\frac{(\text{NEP})_{\min}}{\nu^{1/2}} = \alpha T_0 \mathcal{G}^{1/2}, \quad \alpha \sim 1, \quad (5.45)$$

is reached at $\nu\tau \approx 1$. (The exact values of the optimal product $\omega\tau$, and the numerical constant $\alpha \sim 1$ in Eq. (45), depend on the exact law of power modulation in time, and the output signal processing procedure.) With the parameters cited above, this estimate yields $(\text{NEP})_{\min}/\nu^{1/2} \sim 3 \times 10^{-17}$ W/Hz^{1/2} – a very low power indeed.

⁸ Besides low internal electric noise, the sensor should have a sufficiently large *temperature responsivity* dR/dT , making the noise contribution by the pickup electronics insignificant – see below.

However, surprisingly enough, the power modulation allows bolometric (and other broadband) receivers to register radiation with power much lower than this NEP! Indeed, picking up the sensor signal at the modulation frequency ω , we can use the following electronics stages to filter out all the noise besides its components within a very narrow band, of width $\Delta\nu \ll \nu$, around the modulation frequency (Fig. 7). This is the idea of a *microwave radiometer*,⁹ currently used in all sensitive broadband receivers.

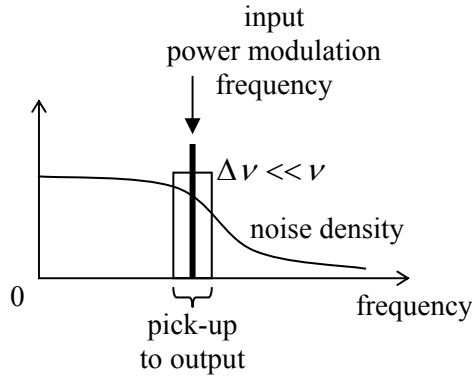


Fig. 5.7. Basic idea of the Dicke radiometer.

In order to analyze this opportunity, we need to develop theoretical tools for a quantitative description of the spectral distribution of fluctuations. Another motivation for that description is the need in analysis of variables dominated by fast (high-frequency) components, such as pressure – please have one more look at Fig. 4. Finally, during the analysis, we will run into the fundamental relation between fluctuations and dissipation, which is one of the main results of statistical physics as a whole.

5.4. Fluctuations as functions of time

There are two mathematically-equivalent approaches to time-dependent functions of time, called *time-domain* and *frequency-domain* pictures, with their relative convenience depending on the particular problem to be solved.

In the time domain, we cannot characterize a random fluctuation $\tilde{f}(t)$ of a classical variable by its statistical average, because it equals zero – see Eq. (2). Of course, variance (3) does not vanish, but if fluctuations are *stationary*, it does not depend on time either. Because of that, let us consider the following average:¹⁰

$$\langle \tilde{f}(t) \tilde{f}(t') \rangle. \quad (5.46)$$

Generally, this is a function of two arguments. Moreover, in the systems that are *stationary* (whose macroscopic parameters and hence the variable expectation values do not change with time), averages like (46) may depend only on the difference,

$$\tau \equiv t' - t, \quad (5.47)$$

⁹ It was pioneered in the 1950s by R. Dicke, so that the device is frequently called the *Dicke radiometer*.

¹⁰ Clearly, this is a temporal analog of the spatial correlation function discussed in Sec. 4.2 – see Eq. (4.30).

between the two observation times. In this case, average (46) is called the *correlation function* of variable f :

$$K_f(\tau) \equiv \langle \tilde{f}(t) \tilde{f}(t + \tau) \rangle. \quad (5.48) \quad \text{Correlation function}$$

This name¹¹ catches the idea of this notion very well: $K_f(\tau)$ tells us about the average mutual relation between the fluctuations at two times separated by interval τ . Let us list the basic properties of this function.

First of all, $K_f(\tau)$ has to be an even function of the time delay τ . Indeed, we may write

$$K_f(-\tau) = \langle \tilde{f}(t) \tilde{f}(t - \tau) \rangle = \langle \tilde{f}(t - \tau) \tilde{f}(t) \rangle = \langle \tilde{f}(t') \tilde{f}(t' + \tau) \rangle, \quad (5.49)$$

with $t' \equiv t - \tau$. For stationary processes, this average cannot depend on the common shift t' of the two observation times, so that averages (48) and (49) have to be equal:

$$K_f(-\tau) = K_f(\tau). \quad (5.50)$$

Second, at $\tau \rightarrow 0$ the correlation function tends to the variance:

$$K_f(0) = \langle \tilde{f}(t) \tilde{f}(t) \rangle = \langle \tilde{f}^2 \rangle. \quad (5.51)$$

In the opposite limit, when τ is much larger than some characteristic *correlation time* τ_c of the system,¹² the correlation function tends to zero, because fluctuations separated by such large time interval are virtually independent (*uncorrelated*). As a result, the correlation function typically looks like one of the plots sketched in Fig. 8. Note that on a time scale much longer than τ_c , any physically-realistic correlation function may be well approximated with a delta-function of τ .¹³

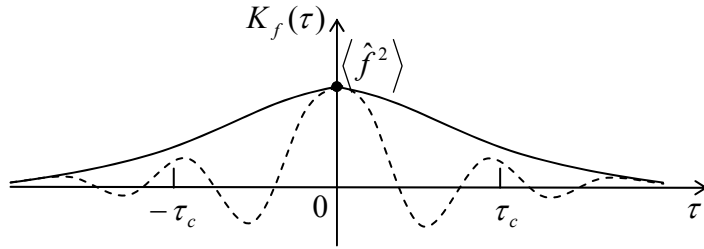


Fig. 5.8. Correlation function of fluctuations: two typical examples.

In the reciprocal, frequency domain, process $\tilde{f}(t)$ is presented as a Fourier integral,

$$\tilde{f}(t) = \int_{-\infty}^{+\infty} f_{\omega} e^{-i\omega t} d\omega, \quad (5.52)$$

with the reciprocal transform being

¹¹ Another term, the *autocorrelation function*, is sometimes used for average (48) to distinguish it from the *mutual correlation function*, $\langle f(t)g(t + \tau) \rangle$, of two stationary processes.

¹² Correlation time τ_c is the direct temporal analog of the correlation radius r_c which was discussed in Sec. 4.2.

¹³ For example, for a process which is a sum of independent very short pulses, e.g., the gas pressure force exerted on the container wall (Fig. 4), such approximation is legitimate on time scales longer than the single pulse duration, e.g., the time of particle's impact on the wall.

$$f_{\omega} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{f}(t) e^{i\omega t} dt. \quad (5.53)$$

If the initial function $\tilde{f}(t)$ is random (as it is in the case of fluctuations), with zero average, its Fourier transform f_{ω} is a random function (now of frequency) as well, also with a vanishing statistical average:

$$\langle f_{\omega} \rangle = \left\langle \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{f}(t) e^{i\omega t} dt \right\rangle = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \langle \tilde{f}(t) \rangle e^{i\omega t} dt = 0. \quad (5.54)$$

The simplest nonvanishing average may be formed similarly to Eq. (46), but with due respect to the complex-variable character of the Fourier images:

$$\langle f_{\omega} f_{\omega'}^* \rangle = \frac{1}{(2\pi)^2} \int_{-\infty}^{+\infty} dt' \int_{-\infty}^{+\infty} dt \langle \tilde{f}(t) \tilde{f}(t') \rangle e^{i(\omega t' - \omega t)}. \quad (5.55)$$

It turns out that for a stationary process, averages (46) and (55) are directly related. Indeed, since the integration over t' in Eq. (55) is in infinite limits, we may replace it with integration over $\tau \equiv t' - t$ (at fixed t), also in infinite limits. Replacing t' by $t + \tau$ in expressions under the integral, we see that the average is just the correlation function $K_f(\tau)$, while the time exponent is equal to $\exp\{i(\omega' - \omega)t\} \exp\{i\omega'\tau\}$. As a result, changing the order of integration, we get

$$\langle f_{\omega} f_{\omega'}^* \rangle = \frac{1}{(2\pi)^2} \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} d\tau K_f(\tau) e^{i(\omega - \omega')t} e^{i\omega'\tau} = \frac{1}{(2\pi)^2} \int_{-\infty}^{+\infty} K_f(\tau) e^{i\omega'\tau} d\tau \int_{-\infty}^{+\infty} e^{i(\omega - \omega')t} dt. \quad (5.56)$$

But the last integral is just $2\pi\delta(\omega - \omega')$,¹⁴ so that we finally get

Spectral
density of
fluctuations

$$\langle f_{\omega} f_{\omega'}^* \rangle = S_f(\omega) \delta(\omega - \omega'), \quad (5.57)$$

where the real function of frequency,

$$S_f(\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{+\infty} K_f(\tau) e^{i\omega\tau} d\tau = \frac{1}{\pi} \int_0^{\infty} K_f(\tau) \cos \omega\tau d\tau, \quad (5.58)$$

Wiener-
Khinchin
theorem

is called the *spectral density of fluctuations at frequency ω* . According to Eq. (58), the spectral density is a Fourier image of the correlation function, and hence the reciprocal Fourier transform is:^{15,16}

$$K_f(\tau) = \int_{-\infty}^{+\infty} S_f(\omega) e^{-i\omega\tau} d\omega = 2 \int_0^{\infty} S_f(\omega) \cos \omega\tau d\omega. \quad (5.59)$$

In particular, for the variance, Eq. (59) yields

¹⁴ See, e.g., MA Eq. (14.4a).

¹⁵ The second form of Eq. (59) uses the fact that, according to Eq. (58), $S_f(\omega)$ is an even function of frequency - just as $K_f(\tau)$ is an even function of time.

¹⁶ Although Eqs. (58) and (59) look not much more than straightforward corollaries of the Fourier transform, they bear a special name of the *Wiener-Khinchin theorem* - after mathematicians N. Wiener and A. Khinchin who have proved that these relations are valid even for functions $f(t)$ which are not square-integrable, so that from the point of view of rigorous mathematics, their Fourier transforms are not well defined.

$$\langle \tilde{f}^2 \rangle = K_f(0) = \int_{-\infty}^{+\infty} S_f(\omega) d\omega = 2 \int_0^{\infty} S_f(\omega) d\omega. \quad (5.60)$$

This relation shows that term “spectral density” describes the physical sense of function $S_f(\omega)$ very well. Indeed, if a random signal $f(t)$ had been passed through a frequency filter with a small bandwidth $\Delta\nu \ll \nu$ of positive cyclic frequencies, the integral in Eq. (60) had to be limited to interval $\Delta\omega = 2\pi\Delta\nu$, i.e. that the variance of the output signal would become¹⁷

$$\langle \tilde{f}^2 \rangle_{\Delta\nu} = 2S_f(\omega)\Delta\omega = 4\pi S_f(\omega)\Delta\nu. \quad (5.61)$$

To complete this introductory section, let me note an important particular case. If the spectral density of some process, is nearly constant within the frequency range of interest, $S_f(\omega) = \text{const} = S_f(0)$,¹⁸ Eq. (59) shows that its correlation function may be well approximated by a delta-function:

$$K_f(\tau) = S_f(0) \int_{-\infty}^{+\infty} e^{-i\omega\tau} d\omega = 2\pi S_f(0) \delta(\tau). \quad (5.62)$$

From this relation stems another popular name of the white noise, the *delta-correlated process*. We have already seen that this is a very reasonable approximation, for example, for the gas pressure force fluctuations (Fig. 4). Of course, for spectral density of a realistic, limited physical variable the approximation of constant spectral density cannot be true for *all* frequencies (otherwise, for example, integral (60) would diverge, giving an unphysical, infinite value of variance), and is valid only at frequencies much lower than $1/\tau_c$.

5.5. Fluctuations and dissipation

Now we are mathematically equipped to address one of the most important topics of statistical physics, the relation between fluctuations and dissipation. This relation is especially simple for the following hierarchical situation: a relatively “heavy”, slowly moving system interacting with an environment consisting of rapidly moving, “light” components. A popular theoretical term for such a system is the *Brownian particle*, named after botanist R. Brown who first noticed in 1827 the random motion of pollen grains, caused by their random hits by fluid molecules, under a microscope. However, the family of such systems is much broader than that of mechanical particles.¹⁹

One more important assumption of this theory is that the system’s motion does not violate the thermal equilibrium of the environment - well fulfilled in many cases. (Think, for example, about a usual mechanical pendulum whose motion does not overheat the air around it.) In this case, the statistical averaging over the thermally-equilibrium environment may be performed for any (slow)

¹⁷ A popular alternative definition of the spectral density is $\mathcal{S}_f(\nu) \equiv 4\pi S_f(\omega)$, making average (61) equal to $\mathcal{S}_f(\nu)\Delta\nu$.

¹⁸ Such process is frequently called *white noise*, because it consists of all frequency components with equal amplitudes, reminding the white light, which consists of many monochromatic components.

¹⁹ Just for one example, such description may be valid for the complex amplitude of an electromagnetic field mode weakly interacting with matter. To emphasize this generality, I will use letter q rather than x for “particle’s” coordinate.

motion of the system of interest, considering the motion fixed.²⁰ I will denote such a “primary” averaging by angular brackets $\langle \dots \rangle$. At a later stage we may carry out another, “secondary” averaging, over an ensemble of many similar systems of interest, coupled to similar environments. If we do, it will be denoted by double angle brackets $\langle \langle \dots \rangle \rangle$.

Let me start from a simple classical system, a 1D harmonic oscillator whose equation of evolution may be presented as

$$m\ddot{q} + \kappa q = \mathcal{F}_{\text{det}}(t) + \mathcal{F}_{\text{env}}(t) = \mathcal{F}_{\text{det}}(t) + \langle \mathcal{F} \rangle + \tilde{\mathcal{F}}(t), \quad (5.63)$$

where q is the (generalized) coordinate of the oscillator, $\mathcal{F}_{\text{det}}(t)$ is the deterministic (generalized) external force, while both components of the random force $\mathcal{F}(t)$ present the impact of the environment on oscillator’s motion. Again, from the point of view of the fast-moving environmental components, the oscillator’s motion is slow. The average of the force exerted by environment on such a slowly moving object may have a part depending on not only q , but on the velocity $\dot{q}$ as well. For most systems, the Taylor expansion of the force in small velocity would have a finite leading, linear term, so that we may take

$$\langle \mathcal{F} \rangle = -\eta \dot{q}, \quad (5.64)$$

so that Eq. (63) may be rewritten as

Langevin
equation
for classical
oscillator

$$m\ddot{q} + \eta \dot{q} + \kappa q = \mathcal{F}_{\text{det}}(t) + \tilde{\mathcal{F}}(t). \quad (5.65)$$

This way of describing the effects of environment on an otherwise Hamiltonian system is called the *Langevin equation*.²¹ Due to the linearity of the differential equation (65), its general solution may be presented as a sum of two parts: the deterministic motion of the linear oscillator due to the external force $\mathcal{F}_{\text{det}}(t)$, and random fluctuations due to the random force exerted by the environment. The former effects are well known from classical dynamics,²² so let us focus on the latter part by taking $\mathcal{F}_{\text{det}}(t) = 0$. The remaining term in the right-hand part describes the fluctuating part of the environmental force; in contrast to the average component (64), its intensity (read: its spectral density at relevant frequencies $\omega \sim \omega_0 \equiv (\kappa/m)^{1/2}$) does not vanish at $q(t) = 0$, and hence may be evaluated ignoring system’s motion.

Plugging into Eq. (65) the presentation of both variables in the form similar to Eq. (52), for their Fourier images we get the following relation:

$$-m\omega^2 q_\omega - i\omega\eta q_\omega + \kappa q_\omega = \tilde{\mathcal{F}}_\omega. \quad (5.66)$$

which immediately gives us q_ω :

²⁰ For a usual (ergodic) environment, the primary averaging may be interpreted as that over relatively short time intervals, $\tau_c \ll \Delta t \ll \tau$, where τ_c is the correlation time of the environment, while τ is the characteristic time scale of motion of our “heavy” system of interest.

²¹ After P. Langevin whose 1908 work was the first systematic development of A. Einstein’s ideas on Brownian motion (see below) using this formalism. A detailed discussion of this approach, with numerical examples of its application, may be found, e.g., in the monograph by W. Coffey, Yu. Kalmykov, and J. Waldron, *The Langevin Equation*, World Scientific, 1996.

²² See, e.g., CM Sec. 4.1. In this and the next sections I assume that variable $f(t)$ is classical, with the discussion of the quantum case postponed until Sec. 6.

$$q_\omega = \frac{\mathcal{F}_\omega}{(\kappa - m\omega^2) - i\eta\omega}. \quad (5.67)$$

Now multiplying Eq. (67) by its complex conjugate, averaging both parts of the resulting equation, and using for each of them Eq. (57),²³ we get the following relation between spectral densities of the oscillations and force:

$$S_q(\omega) = \frac{1}{(\kappa - m\omega^2)^2 + (\eta\omega)^2} S_{\mathcal{F}}(\omega). \quad (5.68)$$

As the reader should know well from classical dynamics, at small damping ($\eta \ll m\omega_0$) the first factor in the right-hand part of Eq. (68) describes the *resonance*, i.e. has a sharp peak near oscillator's eigenfrequency ω_0 , and may be presented in that vicinity as

$$\frac{1}{(\kappa - m\omega^2)^2 + (\eta\omega)^2} \approx \frac{1}{4m\kappa(\xi^2 + \delta^2)}, \quad \text{at } |\xi| \ll \omega_0 \quad \text{with } \xi \equiv \omega - \omega_0, \quad \delta \equiv \eta/2m. \quad (5.69)$$

In contrast, spectral density $S_{\mathcal{F}}(\omega)$ of fluctuations of a typical environment is changing slowly near that frequency, so that for the purpose of integration over frequencies near ω_0 we may replace $S_{\mathcal{F}}(\omega)$ with $S_{\mathcal{F}}(\omega_0)$. As a result, the variance of the environment-imposed random oscillations may be calculated as

$$\langle\langle \tilde{q}^2 \rangle\rangle = 2 \int_0^\infty S_q(\omega) d\omega \approx 2 \int_{\omega \approx \omega_0} S_q(\omega) d\omega \approx 2 S_{\mathcal{F}}(\omega_0) \frac{1}{4m\kappa} \int_{-\infty}^{+\infty} \frac{d\xi}{\xi^2 + \delta^2}. \quad (5.70)$$

The last expression includes a well-known table integral,²⁴ equal to $\pi/\delta = 2\pi m/\eta$, so that finally

$$\langle\langle \tilde{q}^2 \rangle\rangle = 2 S_{\mathcal{F}}(\omega_0) \frac{1}{4m\kappa} \frac{2\pi m}{\eta} = \frac{\pi}{\kappa\eta} S_{\mathcal{F}}(\omega_0). \quad (5.71)$$

But on the other hand, the weak interaction with environment should keep the oscillator in thermodynamic equilibrium at the same temperature T . Since our analysis has been based on the classical Langevin equation (65), we may only use it in the classical limit $\hbar\omega_0 \ll T$, in which we may use the equipartition theorem (2.48). In our current notation, it yields

$$\frac{\kappa}{2} \langle\langle \tilde{q}^2 \rangle\rangle = \frac{T}{2}. \quad (5.72)$$

Comparing Eqs. (71) and (72), we see that the spectral density of the random force exerted by environment is fundamentally related to the damping it provides:

$$S_{\mathcal{F}}(\omega_0) = \frac{\eta}{\pi} T. \quad (5.73a)$$

Now we may argue (rather convincingly :-)) that since this relation does not depend on oscillator's parameters m and κ , and hence its eigenfrequency $\omega_0 = (\kappa/m)^{1/2}$, it should be valid at any (but

²³ At this stage we restrict our analysis to random, stationary processes $q(t)$, so that Eq. (57) is valid for this variable as well, if the averaging is understood in the $\langle\langle \dots \rangle\rangle$ sense.

²⁴ See, e.g. MA Eq. (6.5a).

sufficiently low, $\omega\tau_c \ll 1$) frequency. Using Eq. (58) with $\omega \rightarrow 0$, it may be rewritten as a formula for the effective low-frequency viscosity:

No dissipation
without
fluctuations

$$\eta = \frac{1}{T} \int_0^\infty K_{\tilde{\tau}}(\tau) d\tau \equiv \frac{1}{T} \int_0^\infty \langle \tilde{\tau}(0) \tilde{\tau}(\tau) \rangle d\tau. \quad (5.73b)$$

Relation (73) reveals an intimate, fundamental connection between fluctuations and dissipation provided by a thermally-equilibrium environment. Verbally, “there is no dissipation without fluctuations” - and vice versa.²⁵ Historically, this fact was first recognized in 1905 by A. Einstein,²⁶ in the following form. Let us apply our result (73) to the particular case of a free 1D Brownian particle, by taking $\kappa = 0$. In this case both equations (71) and (72) give infinities. In order to understand the reason for that divergence, let us go back to the Langevin equation (65) with not only $\kappa = 0$, but also, just for the sake of simplicity, $m \rightarrow 0$ as well. (The latter approximation, frequently called the *overdamping limit*, is quite appropriate for the motion of a small particle in a viscous fluid, when $m \ll \eta\Delta t$ even for smallest time intervals Δt between the successive observations of particle’s positions.) In this approximation, Eq. (65) is reduced to a simple equation,

$$\eta \dot{q} = \tilde{\tau}_{\text{det}}(t) + \tilde{\tau}(t), \quad (5.74)$$

with a ready solution for particle displacement during a finite time interval t :

$$\Delta q(t) \equiv q(t) - q(0) = \langle \langle \Delta q(t) \rangle \rangle + \tilde{q}(t), \quad \langle \langle \Delta q(t) \rangle \rangle = \frac{1}{\eta} \int_0^t \tilde{\tau}_{\text{det}}(t') dt', \quad \Delta \tilde{q}(t) = \frac{1}{\eta} \int_0^t \tilde{\tau}(t') dt'. \quad (5.75)$$

Evidently, in the statistical average of the displacement, the fluctuation effects vanish, but this does not mean that the particle does not deviate from the deterministic trajectory $\langle \langle q(t) \rangle \rangle$ – just that it has equal probabilities to be shifted either of two possible directions from that trajectory. To see that, let us calculate the variance of the displacement:

$$\langle \langle \Delta \tilde{q}^2(t) \rangle \rangle = \frac{1}{\eta^2} \int_0^t dt' \int_0^t dt'' \langle \tilde{\tau}(t') \tilde{\tau}(t'') \rangle = \frac{1}{\eta^2} \int_0^t dt' \int_0^t dt'' K_{\tilde{\tau}}(t' - t''). \quad (5.76)$$

As we already know, at times $\tau \gg \tau_c$ (this correlation time, for typical molecular impacts, is of the order of a picosecond), correlation function may be well approximated by the delta-function – see Eq. (62). In this approximation, with $S_{\tilde{\tau}}(0)$ expressed by Eq. (73), and Eq. (80) yields

$$\langle \langle \Delta \tilde{q}^2(t) \rangle \rangle = \frac{2\pi}{\eta^2} S_{\tilde{\tau}}(0) \int_0^t dt' \int_0^t dt'' \delta(t - t') = \frac{2\pi}{\eta^2} \frac{\eta T}{\pi} \int_0^t dt' \int_0^t dt'' \delta(t - t') = 2Dt, \quad (5.77)$$

with

²⁵ This means that the phenomenological description of dissipation by bare viscosity in classical mechanics (see, e.g., CM Sec. 4.1) is only valid approximately, when the energy scale of the process is much larger than T .

²⁶ It was published in one of the three papers of Einstein’s celebrated 1905 “triad”. As a reminder, another paper started the (special) relativity, and one more was the quantum description of photoelectric effect, essentially the prediction of light quanta – photons, which essentially started quantum mechanics. (Not too bad for one year!)

$$D = \frac{T}{\eta}.$$

(5.78) Einstein's relation

The final form of Eq. (77) describes the well-known law of *diffusion* (“random walk”) of a 1D system, with the r.m.s. deviation from the point of origin growing as $(2Dt)^{1/2}$. Coefficient D in this relation is called the *coefficient of diffusion*, and Eq. (78) describes the extremely simple *Einstein relation* between that coefficient and particle’s damping. Often this relation is rewritten in SI units of temperature as $D = \mu_m k_B T_K$, where $\mu_m \equiv 1/\eta$ is the *mobility* of the particle. The physical sense of μ_m becomes clear from rewriting the expression for the deterministic viscous motion $\langle\langle q(t) \rangle\rangle$ (particle’s “drift”) in the form:

$$v_{\text{drift}} \equiv \frac{d\langle\langle q(t) \rangle\rangle}{dt} = \frac{1}{\eta} \mathcal{F}_{\text{det}}(t) = \mu_m \mathcal{F}_{\text{det}}(t), \quad (5.79)$$

so that mobility is just velocity given to the particle by unit force.²⁷

Another famous example of application of Eq. (73) is to the *thermal* (or “Johnson”, or “Johnson-Nyquist”, or just “Nyquist”) *noise* in resistive electron devices. Let us consider a two-terminal “probe” circuit, playing the role of the harmonic oscillator in our analysis above, connected to a resistor R (Fig. 9), playing the role of noisy environment. (The noise is generated by the thermal motion of numerous electrons, randomly moving inside the resistor.) For this system, one convenient choice of conjugate variables (the generalized coordinate and generalized force) is, respectively, the electric charge $Q \equiv \int I(t) dt$ that has passed through the “probe” circuit by time t , and voltage $\mathcal{V}$ across its terminals, with the polarity shown in Fig. 9. (Indeed, product $\mathcal{V} dQ$ is indeed the elementary work $d\mathcal{W}$ done by the environment on the probe circuit.)

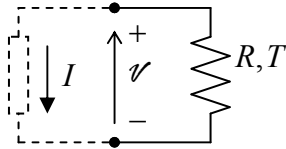


Fig. 5.9. Resistor R of temperature T as a noisy environment of a two-terminal probe circuit.

Making the corresponding replacements, $q \rightarrow Q$ and $\mathcal{F} \rightarrow \mathcal{V}$ in Eq. (64), we see that it becomes

$$\eta \dot{Q} \equiv -\eta I = \langle \mathcal{V} \rangle. \quad (5.80)$$

Comparing this relation with Ohm’s law, $R(-I) = \mathcal{V}$,²⁸ we see that in this case, coefficient η has the physical sense of the usual Ohmic resistance R ,²⁹ so that Eq. (73) becomes

²⁷ In solid-state physics and electronics, mobility is more frequently defined as $|\mathbf{v}_{\text{drift}}/\mathcal{E}| = e|\mathbf{v}_{\text{drift}}/\mathcal{F}_{\text{det}}|$ (where $\mathcal{E}$ is the applied electric field), and is traditionally measured in $\text{cm}^2/\text{V}\cdot\text{s}$. In these units, the electron mobility in silicon wafers used for integrated circuit fabrication (i.e. the solid most important for engineering practice) at room temperature is close to 10^3 .

²⁸ The minus sign is due to the fact that in our notation, current through the resistor equals $(-I)$ – see Fig. 9.

²⁹ Due to this fact, Eq. (64) is often called the *Ohmic model* of the environment response, even if the physical nature of variables q and $\mathcal{F}$ is completely different from the electric charge and voltage.

$$S_{\mathcal{V}}(\omega) = \frac{R}{\pi} T. \quad (5.81a)$$

Using Eq. (61), and transferring to the SI units of temperature ($T \rightarrow k_B T_K$), we can bring this famous *Nyquist formula*³⁰ to its most popular form

Nyquist
formula

$$\langle \tilde{\mathcal{V}}^2 \rangle_{\Delta\nu} = 4k_B T_K R \Delta\nu. \quad (5.81b)$$

Note that according to Eq. (65), this result is only valid at a negligible speed of change of the generalized coordinate q (in this case, negligible current I), i.e. Eq. (81) expresses the voltage fluctuations as would be measured by an ideal *voltmeter*, with an input resistance much higher than R .

On the other hand, applying a different choice of generalized coordinate and force, $q \rightarrow \Phi$, $\mathcal{F} \rightarrow I$ (where $\Phi \equiv \int \mathcal{U}(t) dt$ is the generalized magnetic flux, so that $d\mathcal{W} = Id\Phi$), we get $\eta \rightarrow 1/R$, and Eq. (73) yields the thermal fluctuations of the current through the resistor (as measured by an ideal *ammeter*, i.e. at $\mathcal{V} \rightarrow 0$):

$$S_I(\omega) = \frac{1}{\pi R} T, \quad \text{i.e.} \quad \langle \tilde{I}^2 \rangle_{\Delta\nu} = \frac{4k_B T_K}{R} \Delta\nu. \quad (5.81c)$$

Note that Eqs. (81) are valid for noise in thermal equilibrium only. In electric circuits, which may be readily driven out of equilibrium by applied voltage $\langle \mathcal{V} \rangle$, other types of noise are frequently important, notably the *shot noise*, which arises in short conductors, e.g., tunnel junctions, at applied voltages $\langle \mathcal{V} \rangle \gg T/q$, due to the discreteness of charge carriers.³¹ A straightforward analysis using a simple model, described in the assignment of Exercise Problem 9, shows that this noise may be characterized by current fluctuations with low-frequency spectral density

Schottky
formula

$$S_I(\omega) = \frac{|q\bar{I}|}{2\pi}, \quad \text{i.e.} \quad \langle \tilde{I}^2 \rangle_{\Delta\nu} = 2|q\bar{I}| \Delta\nu, \quad (5.82)$$

where q is the electric charge of a single current carrier. This is the *Schottky formula*, valid for any relation between I and $\mathcal{V}$. Comparison of Eqs. (81c) and (82) for a device that obeys the Ohm law shows that the shot noise has the same intensity as the thermal noise with effective temperature

$$T_{\text{ef}} = \frac{|q\bar{\mathcal{V}}|}{2} \gg T. \quad (5.83)$$

This relation may be interpreted as a result of charge carrier overheating by the applied electric field, and explains why the Schottky formula (82) is only valid in conductors much shorter than the energy

³⁰ Named after H. Nyquist who derived this formula in 1928 (independently of the prior work by A. Einstein, M. Smoluchowski, and P. Langevin) to describe the noise which had been just discovered experimentally by his Bell Labs' colleague J. B. Johnson. The derivation of Eq. (73) and hence Eq. (81) in these notes is essentially a twist of the derivation used by Nyquist.

³¹ Another practically important type of fluctuations in electronic devices is the low-frequency *1/f noise* which was already mentioned in Sec. 3 above. I will briefly discuss it in Sec. 8.

relaxation length l_e of the charge carriers.³² Another mechanism of the shot noise suppression, that becomes noticeable if system's transparency is high, is the Fermi-Dirac statistics of electrons.³³

Returning to the bolometric Dicke radiometer (see Figs. 6-7 and their discussion), we may now use the Langevin equation formalism to finalize its analysis. For this system, the Langevin equation is just the usual equation of heat balance:

$$C_V \frac{dT}{dt} + \mathcal{G}(T - T_0) = \mathcal{P}_{\text{det}}(t) + \tilde{\mathcal{P}}(t), \quad (5.84)$$

where $\mathcal{P}_{\text{det}} = \langle \mathcal{P} \rangle$ describes the (deterministic) power of absorbed radiation, and $\tilde{\mathcal{P}}$ presents the effective source of temperature fluctuations. Now we can use Eq. (84) to carry out a calculation of the spectral density $S_T(\omega)$ of temperature fluctuations absolutely similar to how this was done with Eq. (65), assuming that the frequency spectrum of the fluctuation source is much broader than the intrinsic bandwidth $1/\tau = \mathcal{G}/C_V$ of the bolometer, so that its spectral density at frequencies $\omega\tau \sim 1$ may be well approximated by its low-frequency value $S_{\mathcal{P}}(0)$:

$$S_T(\omega) = \left| \frac{1}{-i\omega C_V + \mathcal{G}} \right|^2 S_{\mathcal{P}}(0). \quad (5.85)$$

Then, requiring the variance of temperature fluctuations,

$$(\delta T)^2 \equiv \langle \tilde{T}^2 \rangle = 2 \int_0^\infty S_T(\omega) d\omega = 2 S_{\mathcal{P}}(0) \int_0^\infty \left| \frac{1}{-i\omega C_V + \mathcal{G}} \right|^2 d\omega = 2 S_{\mathcal{P}}(0) \frac{1}{C_V^2} \int_0^\infty \frac{d\omega}{\omega^2 + (\mathcal{G}/C_V)^2} = \frac{\pi S_{\mathcal{P}}(0)}{\mathcal{G} C_V}, \quad (5.86)$$

to coincide with our earlier “thermodynamic fluctuation” result (41), we get

$$S_{\mathcal{P}}(0) = \frac{\mathcal{G}}{\pi} T_0^2. \quad (5.87)$$

The r.m.s. value of the “power noise” $\tilde{\mathcal{P}}$ within bandwidth $\Delta\nu \ll 1/\tau$ (Fig. 7) becomes equal to the deterministic signal power $\mathcal{P}_{\text{det}}$ (or more exactly, the main harmonic of its modulation law) at

$$\mathcal{P}_{\text{min}} = \left(\langle \tilde{\mathcal{P}}^2 \rangle_{\Delta\nu} \right)^{1/2} = (2 S_{\mathcal{P}}(0) \Delta\omega)^{1/2} = 2(\mathcal{G} \Delta\nu)^{1/2} T_0. \quad (5.88)$$

This result shows that our earlier prediction (45) may be improved by a substantial factor of the order of $(\Delta\nu/\nu)^{1/2}$, where the reduction of the output bandwidth is limited only by the signal accumulation time $\Delta t \sim 1/\Delta\nu$, while the increase of ν is limited by the speed of (typically, mechanical) devices performing the power modulation. In practical systems this factor may improve the sensitivity by a couple orders of magnitude, enabling observation of extremely weak radiation. Maybe the most spectacular example are the recent measurements of the CMB radiation (discussed in Sec. 2.6), which corresponds to blackbody temperature $T_K \approx 2.725$ K, with accuracy $\delta T_K \sim 10^{-6}$ K, using microwave

³² See, e.g., Y. Naveh *et al.*, *Phys. Rev. B* **58**, 15371 (1998). In practically used metals, l_e is of the order of 30 nm even at liquid helium temperatures (and even shorter at ambient conditions), so that the usual “macroscopic” resistors do not exhibit the shot noise.

³³ For a review of this effect see, e.g., Ya. Blanter and M. Büttiker, *Phys. Repts.* **336**, 1 (2000).

receivers with physical temperature of all their components much higher than δT . The observed weak ($\sim 10^{-5}$ K) anisotropy of the CMB radiation is a major experimental basis of all modern cosmology.

Let me also note that Eq. (73) may be readily generalized to the case when environment's response is different from the Ohmic model (64). This generalization is virtually evident from Eq. (66). Indeed, the second term in its left-hand part is just the Fourier component of the average response of the environment:

$$\langle \hat{\mathcal{F}}_\omega \rangle = i\omega\eta q_\omega. \quad (5.89)$$

Let the environment's response be still linear, but have an arbitrary dispersion,

$$\langle \hat{\mathcal{F}}_\omega \rangle = \chi(\omega)q_\omega, \quad (5.90)$$

where the function $\chi(\omega)$, called the *generalized susceptibility* of the environment, may be complex, i.e. have both the imaginary and real parts:

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega). \quad (5.91)$$

Then Eq. (73) remains valid³⁴ with the replacement $\eta \rightarrow \chi''(\omega)/\omega$:

$$S_{\hat{\mathcal{F}}}(\omega) = \frac{\chi''(\omega)}{\pi\omega} T. \quad (5.92)$$

This fundamental relation³⁵ is used not only to calculate the fluctuation intensity from the known generalized responsibility (i.e. the deterministic response of a complex system to a small perturbation), but sometimes in the opposite direction – to calculate the linear response from the known fluctuations. (The latter use is especially attractive at numerical simulations, such as molecular dynamics approaches, because it allows to avoid filtering a weak response from the noisy background.)

Now let us discuss what generalization of Eq. (92) is necessary to make that fundamental result suitable for arbitrary temperatures, $T \sim \hbar\omega$. The calculations we had performed started from the apparently classical equation of motion, Eq. (63). However, quantum mechanics shows³⁶ that a similar equation is valid for the corresponding Heisenberg-picture operators, so that repeating all arguments leading to the Langevin equation (65), we may write its quantum-mechanical version

Heisenberg-
Langevin
equation

$$m\ddot{\hat{q}} + \eta\dot{\hat{q}} + \kappa\hat{q} = \hat{\mathcal{F}}_{\text{det}} + \hat{\mathcal{F}}. \quad (5.93)$$

³⁴ Reviewing the calculations leading to Eq. (73), we may see that if the possible real part $\chi'(\omega)$ of the susceptibility just adds up to $(k - m\omega^2)$ in the denominator of Eq. (67), resulting in a change of oscillator's eigenfrequency. This renormalization is insignificant if the oscillator-to-environment coupling is weak, i.e. susceptibility $\chi(\omega)$ small, as had been assumed at the derivation of Eq. (69) and hence Eq. (73).

³⁵ It is sometimes called the *Green-Kubo* (or just “Kubo”) *formula*. This is hardly fair, because, as the reader could see, Eq. (92) is just an elementary generalization of the Nyquist formula (81). Moreover, the corresponding works of M. Green and R. Kubo were published, respectively, in 1954 and 1957, i.e. after the 1950 paper by H. Callen and T. Welton, where a more general result (see below) had been derived. More adequately, the Green / Kubo names are associated with a related relation between the response function and the operator commutator – see, e.g., QM Eq. (7.109).

³⁶ See, e.g., QM Sec. 4.6.

This is the so-called the *Heisenberg-Langevin* (or “quantum Langevin”) *equation* – in this particular case, for a harmonic oscillator.

The further operations, however, require certain caution, because the right-hand part of the equation is now an operator, and has some nontrivial properties. For example, the “values” of the Heisenberg operator, representing the same variable $f(t)$ at different times, do not necessarily commute:

$$\left[\hat{f}(t), \hat{f}(t') \right] \neq 0, \quad \text{if } t' \neq t. \quad (5.94)$$

As a result, the function defined by Eq. (46) may not be an even function of time delay $\tau \equiv t' - t$ even for a stationary process, making it inadequate for representation of the real correlation function - which has to obey Eq. (51). This technical difficulty may be circumvented by the introduction of the following *symmetrized correlation function*

$$K_f(\tau) \equiv \frac{1}{2} \left\langle \hat{f}(t) \hat{f}(t+\tau) + \hat{f}(t+\tau) \hat{f}(t) \right\rangle \equiv \frac{1}{2} \left\langle \left\{ \hat{f}(t), \hat{f}(t+\tau) \right\} \right\rangle, \quad (5.95)$$

(where $\{\dots, \dots\}$ denotes the anticommutator of the two operators), and, similarly, the symmetrical spectral density $S_f(\omega)$, defined by relation

$$S_f(\omega) \delta(\omega - \omega') \equiv \frac{1}{2} \left\langle \hat{f}_\omega \hat{f}_{\omega'}^* + \hat{f}_{\omega'}^* \hat{f}_\omega \right\rangle \equiv \frac{1}{2} \left\langle \left\{ \hat{f}_\omega, \hat{f}_{\omega'}^* \right\} \right\rangle, \quad (5.96)$$

with $K_f(\tau)$ and $S_f(\omega)$ still related by the Fourier transform (59).³⁷

Now we may repeat all the analysis that was carried out for the classical case, and get Eq. (71) again, but this expression has to be compared not with the equipartition theorem (72), but with its quantum-mechanical generalization (2.78), which, in our current notation, reads

$$\left\langle \left\langle \tilde{q}^2 \right\rangle \right\rangle = \frac{\hbar \omega_0}{2\kappa} \coth \frac{\hbar \omega_0}{2T}. \quad (5.97)$$

As a result, we get the following quantum-mechanical generalization of Eq. (92):

$$S_{\tilde{q}}(\omega) = \frac{\hbar \chi''(\omega)}{2\pi} \coth \frac{\hbar \omega}{2T}. \quad (5.98)$$

Fluctuation-
dissipation
theorem

This is the much-celebrated *fluctuation-dissipation theorem*, frequently referred to just as FDT.³⁸

As natural as it seems, this generalization poses a very interesting conceptual dilemma. Let, for the sake of clarity, temperature be relatively low, $T \ll \hbar \omega$, then Eq. (98) gives a temperature-independent result

$$S_{\tilde{q}}(\omega) = \frac{\hbar \chi''(\omega)}{2\pi}, \quad (5.99)$$

³⁷ Please note that here (and to the end of this section) brackets $\langle \dots \rangle$ mean *quantum*-statistical averaging (2.12). As was discussed in Sec. 2.1, for a classical-mixture state of the environment, this does not create any difference in either mathematical treatment of the averages or their physical interpretation.

³⁸ It was first derived in 1951 by H. Callen and T. Welton (in a somewhat different way). One more derivation of the FDT, which gives the Kubo formula as a by-product, may be found in QM Sec. 7.4.

which is frequently called the *quantum noise*. According to the quantum Langevin equation (93), nothing but these fluctuations of the force exerted by the environment, with spectral density proportional to the imaginary part of susceptibility (i.e. damping), are the source of the ground-state “fluctuations” of the coordinate and momentum of a quantum harmonic oscillator, with r.m.s. values

$$\delta q \equiv \langle \langle \tilde{q}^2 \rangle \rangle^{1/2} = \left(\frac{\hbar}{2m\omega_0} \right)^{1/2}, \quad \delta p \equiv \langle \langle \tilde{p}^2 \rangle \rangle^{1/2} = m\omega_0 \delta q = \left(\frac{\hbar m\omega_0}{2} \right)^{1/2}, \quad \text{i.e. } \delta q \cdot \delta p = \frac{\hbar}{2}, \quad (5.100)$$

and average energy $\hbar\omega_0/2$. On the other hand, the basic quantum mechanics tells us that exactly these formulas describe the ground state of a *dissipation-free* oscillator, not coupled to any environment, and are a direct corollary of the Heisenberg uncertainty relation

$$\delta q \cdot \delta p \geq \frac{\hbar}{2}. \quad (5.101)$$

(The Gaussian wave packets, pertinent to a harmonic oscillator’ ground state, turn the sign in Eq. (101) into pure equality.) So, what is the genuine source of Eqs. (100)?

The resolution of this paradox is that *either* interpretation of Eqs. (100) is legitimate, with their relative convenience depending on the particular application. (One can say that since the right-hand part of the quantum Langevin equation (93) is a quantum-mechanical operator, rather than a classical force, it “carries the uncertainty relation within itself”.) However, this opportunistic resolution leaves the following question open: is the quantum noise (99) of the environment observable directly, without any probe oscillator subjected to it? An experimental resolution of this dilemma is not quite simple, because usual scientific instruments have their own zero-point fluctuations, which may be readily confused with those of the system under study. Fortunately, this difficulty may be overcome, for example, using unique frequency-mixing (“down-conversion”) properties of Josephson junctions.³⁹ Special low-temperature experiments using such down-conversion⁴⁰ have confirmed that noise (99) is real and measurable. This has been one of the most convincing direct demonstrations of the reality of the zero-point energy $\hbar\omega/2$.⁴¹

Finally, let me mention briefly an alternative derivation⁴² of the fluctuation-theorem from the general quantum mechanics of open systems. This derivation is substantially longer, but gives an interesting sub-product,

$$\left\langle \left[\hat{\mathcal{T}}(t), \hat{\mathcal{T}}(t+\tau) \right] \right\rangle = i\hbar \mathcal{G}(\tau), \quad (5.102)$$

where $\mathcal{G}(\tau)$ is the temporal Green’s function of the environment (as “seen” by the system subjected to the generalized force $\mathcal{T}$), defined by equation

$$\langle \mathcal{T}(t) \rangle = \int_0^\infty \mathcal{G}(\tau) q(t-\tau) d\tau = \int_{-\infty}^t \mathcal{G}(t-t') q(t') dt'. \quad (5.103)$$

³⁹ K. Likharev and V. Semenov, *JETP Lett.* **15**, 442 (1972).

⁴⁰ R. Koch *et al.*, *Phys. Rev. B* **26**, 74 (1982).

⁴¹ Another one is the Casimir effect - see, e.g., QM Sec. 9.1.

⁴² See, e.g., QM Sec. 7.4.

Plugging the Fourier transforms of all three functions participating in Eq. (103) into that relation, it is straightforward to check⁴³ that the Green's function is just the Fourier image of the complex susceptibility $\chi(\omega)$, defined by Eq. (90):

$$\int_0^{\infty} \hat{g}(\tau) e^{i\omega\tau} d\tau = \chi(\omega); \quad (5.104)$$

here 0 is used as a lower limit instead of $(-\infty)$ just to emphasize that due to the causality principle, the Green's function has to be equal zero for $\tau < 0$.

In order to reveal the real beauty of Eq. (102), we may use the Wiener-Khinchin theorem (59) to rewrite the fluctuation-dissipation theorem (98) in a form similar to Eq. (102):

$$\left\langle \left\{ \hat{\tilde{F}}(t), \hat{\tilde{F}}(t+\tau) \right\} \right\rangle = 2K_{\tilde{F}}(\tau), \quad (5.105)$$

where the correlation function $K_{\tilde{F}}(\tau)$ is most simply described by its Fourier transform, equal to $\pi S_{\tilde{F}}(\omega)$:

$$\int_0^{\infty} K_{\tilde{F}}(\tau) \cos \omega\tau d\tau = \frac{\hbar \chi''(\omega)}{2} \coth \frac{\hbar\omega}{2T}. \quad (5.106)$$

The comparison of Eqs. (102) and (104), on one hand, and Eqs (105)-(106), on the other hand, shows that both the commutation and anticommutation properties of the Heisenberg-Langevin force operator at different moments of time are determined by the same generalized susceptibility $\chi(\omega)$, but the average anticommutator also depends on temperature, while the average commutator does not.⁴⁴

5.6. The Kramers problem and the Smoluchowski equation

Returning to the classical case, it is evident that the Langevin equation (65) provides the means not only for the analysis of stationary fluctuations, but also for the description of an arbitrary time evolution of (classical) dynamic systems coupled to their environment - which, again, provides both dissipation and fluctuations. However, this approach suffers from two major handicaps.

First, this equation does enable us to find the statistical average of variable q , and the variance of its fluctuations (i.e., in the common mathematical terminology, the first and second *moments* of the probability distribution) as functions of time, but not the distribution $w(q, t)$ as such. This may not look like a big problem, because in most cases (in particular, in linear systems such as the harmonic oscillator) the distribution is Gaussian – see, e.g., Eq. (2.77).

The second, more painful, drawback of the Langevin approach is that it is instrumental only for the already mentioned “linear” systems - i.e., the systems whose dynamics is described by linear differential equations, such as Eq. (65). However, as we know from classical dynamics, many important problems (for example, the Kepler problem of planetary motion⁴⁵) are reduced to 1D motion in substantially anharmonic potentials $U_{\text{ef}}(q)$, leading to nonlinear equations of motion. If the energy of interaction between the system and its random environment is *bilinear* – i.e. is a product of variables

⁴³ See, e.g., CM Sec. 4.1, part (ii).

⁴⁴ Only explicitly so, because the complex susceptibility of the environment may depend on temperature as well.

⁴⁵ See, e.g., CM Sec. 3.4-3.6.

belonging to these sub-systems (as it is very frequently the case), we may repeat all arguments of the last section to derive the following generalized version of the Langevin equation

$$m\ddot{q} + \eta \dot{q} + \frac{\partial U(q, t)}{\partial q} = \tilde{\mathcal{F}}(t), \quad (5.107)$$

valid for an arbitrary, possibly time-dependent potential $U(q, t)$.⁴⁶ Unfortunately, the solution of this equation may be very hard. Indeed, the Fourier analysis carried out in the last section was essentially based on the linear superposition principle that is invalid for nonlinear equations.

If the fluctuation intensity is low, $|\delta q| \ll \langle q \rangle$, where $\langle q \rangle(t)$ is the deterministic solution of Eq. (107) in the absence of fluctuations, this equation may be linearized⁴⁷ with respect to small fluctuations $\tilde{q} \equiv q - \langle q \rangle$ to get a linear equation,

$$m\ddot{\tilde{q}} + \eta \dot{\tilde{q}} + \kappa(t)\tilde{q} = \tilde{\mathcal{F}}(t), \quad \text{with } \kappa(t) \equiv \frac{\partial^2}{\partial q^2} U(\langle q \rangle(t), t). \quad (5.108)$$

This equation differs from Eq. (65) only by the time dependence of the effective spring constant $\kappa(t)$, and may be solved by the Fourier expansion of both fluctuations and function $\kappa(t)$. Such calculations are somewhat more cumbersome than have been performed above, but may be doable (especially if the unperturbed motion $\langle q \rangle(t)$ is periodic), and sometimes give useful analytical results.⁴⁸

However, some important problems cannot be solved by the linearization. Perhaps, the most apparent example is the so-called *Kramers problem*⁴⁹ of finding the lifetime of a metastable state of a 1D classical system in a potential well separated from the continuum motion region with a potential barrier (Fig. 10).

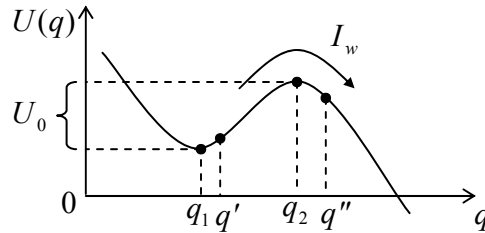


Fig. 5.10. The Kramers problem.

In the absence of fluctuations, the system, placed close to well's bottom ($q = q_1$), would stay there forever. Fluctuations result not only in a finite spread of the probability density $w(q, t)$ around that point, but also in the gradual decrease of the total probability

$$W(t) = \int_{\text{well's bottom}} w(q, t) dq \quad (5.109)$$

⁴⁶ The generalization of Eq. (107) to higher spatial dimensionality is also straightforward, with the scalar variable q replaced by vector $\mathbf{q}$, and the scalar derivative dU/dq replaced with vector ∇U .

⁴⁷ See, e.g., CM Secs. 3.2, 4.2, and beyond.

⁴⁸ See, e.g., Chapters 5 and 6 in W. Coffey *et al.*, *The Langevin Equation*, World Scientific, 1996.

⁴⁹ After H. Kramers who, besides solving this important problem in 1940, has made significant contributions to many other areas of physics, including the famous Kramers-Kronig dispersion relations - see, e.g., EM Sec. 7.4.

to find the system in the well, because of the growing probability of escape from the well, over the potential barrier, due to thermal activation. If the barrier height,

$$U_0 \equiv U(q_2) - U(q_1), \quad (5.110)$$

is much larger than temperature T ,⁵⁰ the Boltzmann distribution $w \propto \exp\{-U(q)/T\}$ should be approximately valid in most of the well, so that the probability for the system to overcome the barrier should scale as $\exp\{-U_0/T\}$. From these handwaving arguments, one may reasonably expect that if probability $W(t)$ that the system is still in the well by time t should obey the usual “decay law”

$$\dot{W} = -\frac{W}{\tau}, \quad (5.111)$$

then lifetime τ has to obey the general Arrhenius law, $\tau = \tau_A \exp\{U_0/T\}$. However, that relation needs to be proved, and the pre-exponential coefficient τ_A (frequently called the *attempt time*) needs to be calculated. This cannot be done by the linearization of Eq. (107), because the linearization is equivalent to a quadratic approximation of the potential $U(q)$, which evidently cannot describe the potential well *and* the potential barrier simultaneously – see Fig. 10.

This and other essentially nonlinear problems may be addressed using an alternative approach to fluctuation analysis, dealing directly with the time evolution of the probability density $w(q,t)$. Due to the shortage of time, I will review this approach a bit superficially, using mostly handwaving arguments, and refer the interested reader to special literature⁵¹ for strict mathematical proofs. Let us start from the effect of diffusion of a *free* 1D particle in the high damping limit, described by the Langevin equation (74), and assume that at all times the probability distribution stays Gaussian:

$$w(q,t) = \frac{1}{(2\pi)^{1/2} \delta q(t)} \exp\left\{-\frac{(q - q_0)^2}{2\delta q^2(t)}\right\}, \quad (5.112)$$

where q_0 is the initial position of the particle, and $\delta q(t)$ is the time-dependent distribution width, which grows in time in accordance with Eq. (77):

$$\delta q(t) = (2Dt)^{1/2}. \quad (5.113)$$

It is straightforward to check, by substitution, that this solution satisfies the following simple partial differential equation,⁵²

$$\frac{\partial w}{\partial t} = D \frac{\partial^2 w}{\partial q^2}, \quad (5.114)$$

with the delta-functional initial condition

$$w(q,0) = \delta(q - q_0). \quad (5.115)$$

⁵⁰ If U_0 is comparable with T , system's behavior also depends substantially on the initial probability distribution, i.e., do not follow the universal law (111).

⁵¹ See, e.g., either R. Stratonovich, *Topics in the Theory of Random Noise*, vol. 1., Gordon and Breach, 1963, or Chapter 1 in the monograph by W. Coffey *et al.*, cited above.

⁵² By the way, the goal of the traditional coefficient 2 in Eq. (77) is exactly to have the fundamental Eq. (114) free of numerical coefficients.

The simple and important *equation of diffusion* (114) may be naturally generalized to the 3D motion:⁵³

Equation
of 3D
diffusion

$$\frac{\partial w}{\partial t} = D \nabla^2 w. \quad (5.116)$$

Now let us compare this equation with the probability conservation law,⁵⁴

$$\frac{\partial w}{\partial t} + \nabla \cdot \mathbf{j}_w = 0, \quad (5.117a)$$

where vector $\mathbf{j}_w$ has the physical sense of the probability current density. (The validity of this relation is evident from its integral form,

$$\frac{d}{dt} \int_V w d^3 r + \oint_S \mathbf{j}_w \cdot d^2 \mathbf{r} = 0, \quad (5.117b)$$

that results from integration of Eq. (117a) over an arbitrary time-independent volume V limited by surface S , and applying the divergence theorem⁵⁵ to the second term.) The continuity relation (117a) coincides with Eq. (116), with D given by Eq. (78), only if we take

$$\mathbf{j}_w = -D \nabla w = -\frac{T}{\eta} \nabla w. \quad (5.118)$$

The first form of this relation allows a simple interpretation: the probability flow is proportional to the spatial gradient of probability density (i.e., in application to many (N) similar and independent particles, just to the gradient of their concentration $n = Nw$), with the sign corresponding to the flow from the higher to lower concentration. This flow is the very essence of the effect of diffusion.

The fundamental Eq. (117) has to be satisfied also for a force-driven particle at negligible diffusion ($D \rightarrow 0$); in this case

$$\mathbf{j}_w = w \mathbf{v}, \quad (5.119)$$

where $\mathbf{v}$ is the deterministic velocity of the particle. In the high-damping limit we are considering right now, $\mathbf{v}$ is just the *drift velocity*:

$$\mathbf{v} = \frac{1}{\eta} \mathcal{F}_{\text{det}} = -\frac{1}{\eta} \nabla U(\mathbf{r}), \quad (5.120)$$

where $\mathcal{F}_{\text{det}}$ is the deterministic force described by potential energy $U(\mathbf{r})$. Now, as we have descriptions of $\mathbf{j}_w$ due to both drift *and* diffusion separately, we may rationally assume that in the general case when both effects are present, the corresponding components of the probability current just add up, so that

$$\mathbf{j}_w = \frac{1}{\eta} [w(-\nabla U) - T \nabla w], \quad (5.121)$$

⁵³ As will be discussed in Chapter 6, the equation of diffusion also describes several other physical phenomena – in particular, heat propagation in a uniform, isotropic solid, and in this context is called the *heat conduction equation* or (rather inappropriately) just the “heat equation”.

⁵⁴ Both forms of Eq. (117) are similar to the mass conservation law in classical dynamics (see, e.g., CM Sec. 8.2), and the electric charge conservation law in electrodynamics (see, e.g., EM Sec. 4.1).

⁵⁵ See, e.g., MA Eq. (12.2),

and Eq. (117a) takes the form

$$\eta \frac{\partial w}{\partial t} = \nabla(w \nabla U) + T \nabla^2 w. \quad (5.122) \quad \text{Smoluchowski equation}$$

This is the *Smoluchowski equation*,⁵⁶ which is closely related to the *Boltzmann equation* in multi-particle kinetics - to be discussed in the next chapter.

As a sanity check, let us see what does the Smoluchowski equation give in the stationary limit, $\partial w / \partial t \rightarrow 0$ (which evidently may be achieved only if the deterministic potential U is time-independent.) Then Eq. (117a) yields $\mathbf{j}_w = \text{const}$, where the constant describes the motion of the system as the whole. If such motion is absent, $\mathbf{j}_w = 0$, then according to Eq. (121),

$$w \nabla U + T \nabla w = 0, \quad \text{i.e.} \quad \frac{\nabla w}{w} = -\frac{\nabla U}{T}. \quad (5.123)$$

Since the left-hand part of the last form of the last relation is just $\nabla(\ln w)$, Eq. (123) may be immediately integrated, giving

$$\ln w = -\frac{U}{T} + \ln C, \quad \text{i.e.} \quad w(\mathbf{r}) = C \exp\left\{-\frac{U(\mathbf{r})}{T}\right\}, \quad (5.124)$$

Multiplied by the number N of similar, independent systems, with spatial density $n(\mathbf{r}) = Nw(\mathbf{r})$, this is just the Boltzmann distribution (3.26).

Now, as a less trivial example of the Smoluchowski equation's applications, let us use it to solve the 1D Kramers problem (Fig. 10) in the corresponding high-damping limit, $m \ll \eta \tau_A$. It is straightforward to check that the 1D version of Eq. (121),

$$I_w = \frac{1}{\eta} \left[w \left(-\frac{\partial U}{\partial q} \right) - T \frac{\partial w}{\partial q} \right], \quad (5.125a)$$

is equivalent to

$$I_w = -\frac{T}{\eta} \exp\left\{-\frac{U(q)}{T}\right\} \frac{\partial}{\partial q} \left(w \exp\left\{\frac{U(q)}{T}\right\} \right), \quad (5.125b)$$

(where I_w is the probability current at a certain location q , rather than its density), so that we can write

$$I_w \exp\left\{\frac{U(q)}{T}\right\} = -\frac{T}{\eta} \frac{\partial}{\partial q} \left(w \exp\left\{\frac{U(q)}{T}\right\} \right). \quad (5.126)$$

As was discussed above, the notion of metastable state's lifetime is well defined only for sufficiently low temperatures

$$T \ll U_0. \quad (5.127)$$

⁵⁶ Named after M. Smoluchowski who developed this formalism in 1906, apparently independently from the slightly earlier Einstein's work, and in much more detail. This equation has important applications in many fields of science, including such surprising topics as statistics of spikes in neural networks.

when the lifetime is relatively long, $\tau \gg \tau_A$, where τ_A has to be of the order of the time of the system relaxation inside the well. Since the first term of the continuity equation (117b) is of the order of W/τ , in this limit the term, and hence the gradient of I_w , are negligibly small, so the probability current does not depend on q in the potential barrier region. Let us integrate both sides of Eq. (126) over that region, using that fact:

$$I_w \int_{q'}^{q''} \exp\left\{\frac{U(q)}{T}\right\} dq = -\frac{T}{\eta} \left(w \exp\left\{\frac{U(q)}{T}\right\} \right)_{q'}^{q''}, \quad (5.128)$$

where the integration limits q' and q'' (Fig. 10) are selected so that so that

$$T \ll U(q') - U(q_1), U(q_2) - U(q'') \ll U_0. \quad (5.129)$$

(Evidently, such selection is only possible if condition (127) is satisfied.) In this limit the contribution to the right-hand part from point q'' is negligible because the probability density behind the barrier is exponentially small. On the other hand, the probability at point q' is close to its stationary, Boltzmann value (124), so that

$$w(q') \exp\left\{\frac{U(q')}{T}\right\} = w(q_1) \exp\left\{\frac{U(q_1)}{T}\right\}, \quad (5.130)$$

and Eq. (128) yields

$$I_w = \frac{T}{\eta} w(q_1) \int_{q'}^{q''} \exp\left\{\frac{U(q) - U(q_1)}{T}\right\} dq. \quad (5.131)$$

We are almost done. The probability density $w(q_1)$ at the well's bottom may be expressed in terms of the total probability W of the particle being in the well by using the normalization condition

$$W = \int_{\text{well's bottom}} w(q_1) \exp\left\{\frac{U(q_1) - U(q)}{T}\right\} dq; \quad (5.132)$$

the integration here may be limited by the region where the difference $U(q) - U(q_1)$ is larger than T but still much smaller than U_0 - cf. Eq. (129). According to the Taylor expansion, the shape of any smooth potential well near its bottom may be well approximated by a quadratic parabola:

$$U(q \approx q_1) - U(q_1) \approx \frac{\kappa_1}{2} (q - q_1)^2, \quad \text{where } \kappa_1 \equiv \frac{d^2 U}{dq^2} \Big|_{q=q_1} > 0. \quad (5.133)$$

With this approximation, Eq. (132) is reduced to the standard Gaussian integral:⁵⁷

$$W = w(q_1) \int_{\text{well's bottom}} \exp\left\{-\frac{\kappa_1 (q - q_1)^2}{2T}\right\} dq \approx w(q_1) \int_{-\infty}^{+\infty} \exp\left\{\frac{\kappa_1 \tilde{q}^2}{2T}\right\} d\tilde{q} = w(q_1) \left(\frac{2\pi T}{\kappa_1}\right)^{1/2}. \quad (5.134)$$

To complete the calculation, we may use the similar approximation,

⁵⁷ If necessary, see MA Eq. (6.9b) again.

$$U(q \approx q_2) - U(q_1) \approx \left[U(q_2) - \frac{\kappa_2}{2} (q - q_2)^2 \right] - U(q_1) = U_0 - \frac{\kappa_2}{2} (q - q_2)^2, \quad (5.135)$$

where $\kappa_2 \equiv -\frac{d^2 U}{dq^2} \Big|_{q=q_2} > 0$,

to work out the remaining integral in Eq. (131), because in the limit (129) this integral is dominated by the contribution from a region very close to the barrier top, where approximation (135) is asymptotically exact. As a result, we get

$$\int_{q'}^{q''} \exp\left\{ \frac{U(q) - U(q_1)}{T} \right\} dq \approx \exp\left\{ \frac{U_0}{T} \right\} \left(\frac{2\pi T}{\kappa_2} \right)^{1/2}. \quad (5.136)$$

Plugging Eqs. (136), and $w(q_1)$ expressed from Eq. (134), into Eq. (131), we finally get

$$I_w = W \frac{(\kappa_1 \kappa_2)^{1/2}}{2\pi\eta} \exp\left\{ -\frac{U_0}{T} \right\}. \quad (5.137)$$

This expression should be compared with the 1D version of Eq. (117b) for the segment $[-\infty, q']$. Since this interval covers the region near q_1 where most of the probability density resides, and $I_q(-\infty) = 0$, the result is merely

$$\frac{dW}{dt} + I_w(q') = 0. \quad (5.138)$$

In our approximation, $I_w(q')$ does not depend on the exact position of point q' , and is given by Eq. (137), so that plugging it into Eq. (138), we recover the exponential decay law (111), with lifetime

$$\tau = \frac{2\pi\eta}{(\kappa_1 \kappa_2)^{1/2}} \exp\left\{ \frac{U_0}{T} \right\} = 2\pi(\tau_1 \tau_2)^{1/2} \exp\left\{ \frac{U_0}{T} \right\}, \quad \text{where } \tau_{1,2} \equiv \frac{\eta}{\kappa_{1,2}}. \quad (5.139)$$

Kramers
formula
for high
damping

Thus the metastable state lifetime is indeed described by the Arrhenius law, with the attempt time scaling as the geometric mean of system's "relaxation times" near the potential well bottom (τ_1) and the potential barrier top (τ_2).⁵⁸ Let me leave for reader's exercise to prove that if the potential profile near well's bottom and/or top is sharp, the pre-exponential factor in Eq. (139) should be modified, but the Arrhenius exponent is not affected.

5.7. The Fokker-Planck equation

Expression (139) is just a particular, high-damping limit of a more general result obtained by Kramers. In order to recover all of it, we need to generalize the Smoluchowski equation to arbitrary values of damping η . In this case, the probability density w is a function of not only the particle's position $\mathbf{q}$ (and time t), but also its momentum $\mathbf{p}$ – see Eq. (2.11). Thus the continuity equation (117a) needs to be generalized to 6D phase space. Such generalization is natural:

⁵⁸ Actually, τ_2 describes the characteristic time of the exponential *growth* of small deviations from the unstable fixed point q_2 at the barrier top, rather than their *decay*, as near point q_1 .

$$\frac{\partial w}{\partial t} + \nabla_q \cdot \mathbf{j}_q + \nabla_p \cdot \mathbf{j}_p = 0, \quad (5.140)$$

where $\mathbf{j}_q$ (which was called $\mathbf{j}_w$ in the last section) is the probability current density in the coordinate space, while $\mathbf{j}_p$ is the current density in the momentum space, and ∇_p is the gradient operator in that space,

$$\nabla_p \equiv \sum_{j=1}^3 \mathbf{n}_j \frac{\partial}{\partial p_j}, \quad (5.141)$$

while ∇_q is the usual gradient operator in the coordinate space, that was denoted as ∇ in the previous section - with index q added here just for additional clarity. At negligible fluctuations ($T \rightarrow 0$), $\mathbf{j}_p$ in the momentum space may be evaluated using the natural analogy with $\mathbf{j}_q$ - see Eq. (119). In our new notation, that relation takes the following form,

$$\mathbf{j}_q = w\mathbf{v} = w\dot{\mathbf{q}} = w\frac{\mathbf{p}}{m}, \quad (5.142)$$

so it is naturally to take

$$\mathbf{j}_p = w\dot{\mathbf{p}} = w\langle \dot{\mathbf{p}} \rangle = w(-\nabla_q U - \eta\mathbf{v}) = w(-\nabla_q U - \eta\frac{\mathbf{p}}{m}). \quad (5.143)$$

As a sanity check, it is straightforward to verify that the diffusion-free equation resulting from the combination of Eqs. (140), (142) and (143),

$$\left. \frac{\partial w}{\partial t} \right|_{\text{drift}} = -\nabla_q \cdot \left(w\frac{\mathbf{p}}{m} \right) + \nabla_p \cdot \left[w \left(\nabla_q U + \eta\frac{\mathbf{p}}{m} \right) \right], \quad (5.144)$$

allows the following particular solution

$$w(\mathbf{q}, \mathbf{p}, t) = \delta(\mathbf{q} - \langle \mathbf{q} \rangle(t)) \delta(\mathbf{p} - \langle \mathbf{p} \rangle(t)), \quad (5.145)$$

where the statistical-average coordinate and momentum satisfy the deterministic equations of motion,

$$\langle \dot{\mathbf{q}} \rangle = \frac{\langle \mathbf{p} \rangle}{m}, \quad \langle \dot{\mathbf{p}} \rangle = -\nabla_q U - \eta\frac{\langle \mathbf{p} \rangle}{m}, \quad (5.146)$$

describing particle's drift, with the appropriate deterministic initial conditions.

In order to understand how the diffusion may be accounted for, let us consider a statistical ensemble of free ($\nabla_q U = 0$, $\eta \rightarrow 0$) particles that are uniformly distributed in direct space (so that $\nabla_q w = 0$), but possibly localized in the momentum space. For this case, the right-hand part of Eq. (144) vanishes, i.e. the time evolution of the probability density w may be only due to diffusion. In the corresponding limit $\langle \mathcal{F} \rangle \rightarrow 0$, the Langevin equation (107) for each Cartesian coordinate is reduced to

$$m\ddot{q}_j = \tilde{\mathcal{F}}_j(t), \quad \text{i.e.} \quad \dot{p}_j = \tilde{\mathcal{F}}_j(t). \quad (5.147)$$

This equation is similar to the high-damping 1D equation (74) (with $\mathcal{F}_{\text{det}} = 0$), with replacement $q \rightarrow p_j/\eta$, and hence the corresponding contribution to $\partial w/\partial t$ may be described by the second term of Eq. (122) with that replacement:

$$\left. \frac{\partial w}{\partial t} \right|_{\text{diffusion}} = D \nabla_p^2 w = \frac{T}{\eta} \eta^2 \nabla_p^2 w = \eta T \nabla_p^2 w. \quad (5.148)$$

Now the reasonable assumption that in the arbitrary case the drift and diffusion contributions to $\partial w / \partial t$ just add up, immediately leads us to the full *Fokker-Planck equation*:⁵⁹

$$\frac{\partial w}{\partial t} = -\nabla_q \cdot \left(w \frac{\mathbf{p}}{m} \right) + \nabla_p \cdot \left[w \left(\nabla_q U + \eta \frac{\mathbf{p}}{m} \right) \right] + \eta T \nabla_p^2 w. \quad (5.149)$$

Fokker-Planck equation

As a sanity check, let us use this equation to find the stationary probability distribution of momentum of free particles, at arbitrary damping η , in the momentum space, assuming their uniform distribution in the direct space, $\nabla_q = 0$. In the stationary case $\partial w / \partial t = 0$, so that Eq. (149) is reduced to

$$\nabla_p \cdot \left[w \left(\eta \frac{\mathbf{p}}{m} \right) \right] + \eta T \nabla_p^2 w = 0. \quad (5.150)$$

The damping coefficient η cancels, and the first integration over momentum yields

$$\frac{\mathbf{p}}{m} w + T \nabla_p w = \mathbf{j}, \quad (5.152)$$

where $\mathbf{j}$ is a vector constant describing a possible motion of the system as the whole. In the absence of such motion, $\mathbf{j} = 0$, the second integration over momentum gives

$$w = \text{const} \times \exp \left\{ -\frac{p^2}{2mT} \right\}, \quad (5.153)$$

i.e. the Maxwell distribution (3.5). However, result (153) is more general than that obtained in Sec. 3.1, because it shows that the distribution stays the same even at nonvanishing damping.

It is also easy to show that if the damping is large (in the sense assumed in the last section), the solution of the Fokker-Planck equation tends to the following product

$$w(\mathbf{q}, \mathbf{p}, t) \rightarrow \text{const} \times \exp \left\{ -\frac{p^2}{2mT} \right\} \times w(\mathbf{q}, t), \quad (5.154)$$

where the direct-space distribution $w(\mathbf{q}, t)$ obeys the Smoluchowski equation (122). However, in the general case, solutions of Eq. (149) may be rather complex,⁶⁰ so I would mention (rather than derive) only one of them, that of the Kramers problem (Fig. 10). Acting virtually exactly as in Sec. 6, one can show at arbitrary damping (but still in the limit (127), $T \ll U_0$, with the additional restriction $\tau \gg m/\gamma$), the metastable state's lifetime is again given by the Arrhenius formula (139), with the same exponent $\exp\{U_0/T\}$, but with the reciprocal time constants $1/\tau_{1,2}$ replaced with

$$\omega'_{1,2} \equiv \left[\omega_{1,2}^2 + \left(\frac{\eta}{2m} \right)^2 \right]^{1/2} - \frac{\eta}{2m} \rightarrow \begin{cases} \omega_{1,2}, & \text{for } \eta \ll m\omega_{1,2}, \\ 1/\tau_{1,2}, & \text{for } m\omega_{1,2} \ll \eta, \end{cases} \quad (5.155)$$

⁵⁹ It was derived in 1913 in A. Fokker's PhD thesis work; M. Planck was his thesis adviser.

⁶⁰ The reader should remember that these solutions embody, as the particular case $T = 0$, all classical dynamics of a particle.

where $\omega_{1,2} \equiv (\kappa_{1,2}/m)^{1/2}$, while $\kappa_{1,2}$ are the effective spring constants defined by Eqs. (133) and (135). Thus, in the most important particular limit of low damping, Eq. (139) is replaced with the famous formula

Kramers
formula
for low
damping

$$\tau = \frac{2\pi}{(\omega_1\omega_2)^{1/2}} \exp\left\{\frac{U_0}{T}\right\}. \quad (5.156)$$

This Kramers' result for the classical thermal activation of the virtually-Hamiltonian system *over* the potential barrier may be compared with that for its quantum-mechanical tunneling *through* the barrier.⁶¹ Even the simplest, WKB approximation for the latter time,

$$\tau_Q = \tau_A \exp\left\{-2 \int_{\kappa^2(q)>0} \kappa(q) dq\right\}, \quad \text{with} \quad \frac{\hbar^2 \kappa^2(q)}{2m} \equiv U(q) - E, \quad (5.157)$$

shows that generally those two lifetimes have different dependences on the barrier shape. For example, for a nearly-rectangular potential barrier, the exponent that determines the classical lifetime (156) depends (linearly) only on the barrier *height* U_0 , while that defining the quantum lifetime is proportional to the barrier *width*, while scaling as a square root of U_0 . However, in the important case of “soft” potential profiles, which are typical for the case of barely emerging (or nearly disappearing) quantum wells (Fig. 11) the classical and quantum results may be simply related.

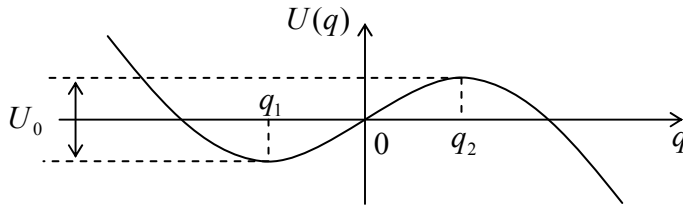


Fig. 5.11. Cubic-parabolic potential profile and its parameters.

Indeed, such potential profile $U(q)$ may be well approximated by 4 leading terms of its Taylor expansion, with the highest term proportional to $(q - q_0)^3$, near some point q_0 in the vicinity of the well. In this approximation, the second derivative d^2U/dq^2 vanishes at the point $q_0 = (q_1 + q_2)/2$, exactly between the well's bottom and the barrier's top (in Fig. 11, q_1 and q_2). Selecting the origin at this point, we may reduce the approximation to just two terms:⁶²

$$U(q) = aq - \frac{b}{3}q^3, \quad (5.158)$$

with $ab > 0$. Using a straightforward calculus, we can find all important parameters of this cubic-parabola: the positions of its minimum and maximum:

$$q_2 = -q_1 = (a/b)^{1/2}, \quad (5.159)$$

the barrier height over the well's bottom:

⁶¹ See, e.g., QM Secs. 2.3-2.4.

⁶² As a reminder, an absolutely similar approximation is used in Exercise Problem 4.3 for the $P(V)$ function, in order to analyze properties of the van der Waals model near the critical temperature.

$$U_0 \equiv U(q_2) - U(q_1) = \frac{4}{3} \left(\frac{a^3}{b} \right)^{1/2}, \quad (5.160)$$

and the effective spring constants:

$$\kappa_1 = \kappa_2 \equiv \left. \frac{d^2 U}{dq^2} \right|_{q_{1,2}} = 2(ab)^{1/2}. \quad (5.161)$$

The last expression shows that for this potential profile, frequencies $\omega_{1,2}$ participating in Eq. (161) are equal to each other, so that this result may be rewritten as

$$\tau = \frac{2\pi}{\omega_0} \exp\left\{ \frac{U_0}{T} \right\}, \quad \text{with } \omega_0^2 \equiv \frac{2(ab)^{1/2}}{m}. \quad (5.162)$$

On the other hand, for the same profile, the WKB approximation (157) (which is accurate when the height of the metastable state energy over the well's bottom, $E - U(q_1) \approx \hbar\omega_0/2$, is much less than the barrier height U_0) yields⁶³

$$\tau_Q = \frac{2\pi}{\omega_0} \left(\frac{\hbar\omega_0}{864\pi U_0} \right)^{1/2} \exp\left\{ \frac{36}{5} \frac{U_0}{\hbar\omega_0} \right\}. \quad (5.163)$$

Comparison of the dominating, exponential factors in these two results shows that the thermal activation yields lower lifetime (i.e., dominates the metastable state decay) if temperature is above the crossover value

$$T_c = \frac{36}{5} \hbar\omega_0 = 7.2 \hbar\omega_0. \quad (5.164)$$

This expression for the *cubic*-parabolic barrier may be compared with the similar crossover for a *quadratic*-parabolic barrier,⁶⁴ for which $T_c = 2\pi \hbar\omega_0 \approx 6.28 \hbar\omega_0$. We see that the numerical factors for these two different soft potential profiles are very substantial, but rather close.

5.8. Back to the correlation function

Unfortunately I will not have time to review solutions of other problems using the Smoluchowski and Fokker-Planck equations, but have to mention one conceptual issue. Since it is intuitively clear that these equations provide the complete statistical information about the system under analysis, one may wonder whether they may be used to find the temporal characteristics of the system, which were discussed in Secs. 4-5 using the Langevin formalism. For any statistical average of a function taken at the same time instant, the answer is evidently *yes* – cf. Eq. (2.11):

$$\langle f(\mathbf{q}(t), \mathbf{p}(t)) \rangle = \int f(\mathbf{q}, \mathbf{p}) w(\mathbf{q}, \mathbf{p}, t) d^3 q d^3 p, \quad (5.165)$$

⁶³ The main, exponential factor in this result may be obtained simply by ignoring the difference between E and $U(q_1)$, but the correct calculation of the pre-exponent requires to take this difference, $\hbar\omega_0/2$, into account – see K. Likharev, *Physica B* **108**, 1079 (1981).

⁶⁴ See, e.g., QM Sec. 2.4.

but what if the function depends on variables taken at *different* times, for example the components of the correlation function $K(\tau)$ defined by Eq. (49)?

To answer this question, let us start from the discrete variable case when Eq. (165) takes form (2.7), which, for our current purposes, may be rewritten as

$$\langle f(t) \rangle = \sum_m f_m W_m(t). \quad (5.166)$$

In plain English, this is a sum of all possible values of the function, each multiplied by its probability as a function of time. But this means that average $\langle f(t)f(t') \rangle$ may be calculated as the sum of all possible products $f_m f_{m'}$, multiplied by the *joint probability* for measurement outcome m at moment t , and outcome m' at moment t' . The joint probability may be presented as a product of $W_m(t)$ by the *conditional probability* $W(m', t' | m, t)$. Since the correlation function is well defined only for stationary systems, in the last expression we can take $t = 0$, i.e. find the conditional probability as the result, $W_m(\tau)$, of solution of the equation describing system's probability evolution, at time $\tau = t' - t$ (rather than t'), with the special initial condition

$$W_{m'}(0) = \delta_{m', m}. \quad (5.167)$$

On the other hand, since the average $\langle f(t)f(t+\tau) \rangle$ of a stationary process should not depend on t , instead of $W_m(t)$ we may take the stationary probability distribution $W_m(\infty)$, independent of the initial conditions, and may be found as the same special solution, but at time $\tau \rightarrow \infty$. As a result, we may write

$$\langle f(t)f(t+\tau) \rangle = \sum_{m, m'} f_m W_m(\infty) f_{m'} W_{m'}(\tau). \quad (5.168)$$

This expression looks simple, but note that this recipe requires to solve the time evolution equations for each $W_m(\tau)$ for all possible initial conditions (167). To see how this recipe works in practice, let us revisit the simplest two-level system (see, e.g., Fig. 4.13 reproduced in Fig. 12 below in a notation more convenient for our current purposes), and calculate the correlation function of its energy fluctuations.

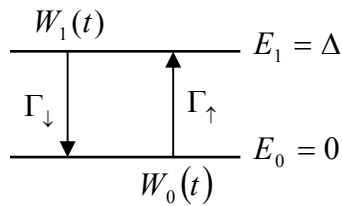


Fig. 5.12. Dynamics of a two-level system.

The stationary probabilities for this system (i.e. the probabilities for $\tau \rightarrow \infty$) have been calculated in Chapter 2, and then again in Sec. 4.4. In our current notation (Fig. 12),

$$W_0(\infty) = \frac{1}{1 + e^{-\Delta/T}}, \quad W_1(\infty) = \frac{1}{e^{\Delta/T} + 1}, \quad \langle E \rangle = W_0(\infty) \times 0 + W_1(\infty) \times \Delta = \frac{\Delta}{e^{\Delta/T} + 1}. \quad (5.169)$$

In order to calculate the conditional probabilities $W_m(\tau)$ with initial conditions (172) (according to Eq. (168), we need all 4 of them, for $m, m' = 0, 1$), we may use master equations (4.100), in our current notation reading

$$\frac{dW_1}{d\tau} = -\frac{dW_0}{d\tau} = \Gamma_{\uparrow}W_0 - \Gamma_{\downarrow}W_1. \quad (5.170)$$

Since Eq. (170) conserves the total probability, $W_0 + W_1 = 1$, only one probability (say, W_1) is an independent variable, and for it, Eq. (170) gives a simple, linear differential equation,

$$\frac{dW_1}{d\tau} = \Gamma_{\uparrow} - \Gamma_{\Sigma}W_1, \quad \text{where } \Gamma_{\Sigma} \equiv \Gamma_{\uparrow} + \Gamma_{\downarrow}. \quad (5.171)$$

This equation may be readily integrated for an arbitrary initial condition:

$$W_1(\tau) = W_1(0)e^{-\Gamma_{\Sigma}\tau} + W_1(\infty)(1 - e^{-\Gamma_{\Sigma}\tau}), \quad (5.172)$$

where $W_1(\infty)$ is given by the second of Eqs. (169). (It is straightforward to check that the solution for $W_0(\tau)$ may be presented in the similar form, with the corresponding change of the state index.) Now everything is ready to calculate average $\langle E(t)E(t+\tau) \rangle$ using Eq. (168), with $f_{m,m'} = E_{0,1}$. Thanks to our (smart :-) choice of energy origin, of 4 terms in the double sum (168), all 3 terms that include at least one factor $E_0 = 0$ vanish, and we have only one term left:

$$\begin{aligned} \langle E(t)E(t+\tau) \rangle &= E_1W_1(\infty)E_1W_1(\tau) \Big|_{W_1(0)=1} = E_1^2W_1(\infty) \left[W_1(0)e^{-\Gamma_{\Sigma}\tau} + W_1(\infty)(1 - e^{-\Gamma_{\Sigma}\tau}) \right] \Big|_{W_1(0)=1} \\ &= \frac{\Delta^2}{e^{\Delta/T} + 1} \left[e^{-\Gamma_{\Sigma}\tau} + \frac{1}{e^{\Delta/T} + 1} (1 - e^{-\Gamma_{\Sigma}\tau}) \right] = \frac{\Delta^2}{(e^{\Delta/T} + 1)^2} (1 + e^{\Delta/T} e^{-\Gamma_{\Sigma}\tau}). \end{aligned} \quad (5.173)$$

From here and the last of Eqs. (169), the correlation function of energy fluctuations is⁶⁵

$$\begin{aligned} K_E(\tau) &\equiv \langle \tilde{E}(t)\tilde{E}(t+\tau) \rangle = \langle (E(t) - \langle E(t) \rangle)(E(t+\tau) - \langle E(t) \rangle) \rangle = \langle E(t)E(t+\tau) \rangle - \langle E(t) \rangle \langle E(t+\tau) \rangle \\ &= \langle E(t)E(t+\tau) \rangle - \langle E \rangle^2 = \Delta^2 \frac{e^{\Delta/T}}{(e^{\Delta/T} + 1)^2} e^{-\Gamma_{\Sigma}\tau}. \end{aligned} \quad (5.174)$$

Since transition rates $\Gamma_{\uparrow}$ and $\Gamma_{\downarrow}$ have to obey the detailed balance relation (4.103), $\Gamma_{\downarrow}/\Gamma_{\uparrow} = \exp\{\Delta/T\}$, and hence

$$\frac{e^{\Delta/T}}{(e^{\Delta/T} + 1)^2} = \frac{\Gamma_{\downarrow}/\Gamma_{\uparrow}}{(\Gamma_{\downarrow}/\Gamma_{\uparrow} + 1)^2} = \frac{\Gamma_{\uparrow}\Gamma_{\downarrow}}{(\Gamma_{\uparrow} + \Gamma_{\downarrow})^2} = \frac{\Gamma_{\uparrow}\Gamma_{\downarrow}}{\Gamma_{\Sigma}^2}, \quad (5.175)$$

expression (174) may be presented also in a simpler form:

$$K_E(\tau) = \Delta^2 \frac{\Gamma_{\uparrow}\Gamma_{\downarrow}}{\Gamma_{\Sigma}^2} e^{-\Gamma_{\Sigma}\tau}. \quad (5.176)$$

We see that the correlation function of energy decays exponentially with time, with the net rate Γ_{Σ} , while its variance, equal to $K_E(0)$, does not depend on the transition rates. Now using the Wiener-Khinchin theorem (58) to calculate its spectral density, we get

Energy fluctuations in two-level system

⁶⁵ The transition from the first line of Eq. (174) to its second one uses the fact that the system is stationary, so that $\langle E(t+\tau) \rangle = \langle E(t) \rangle = \langle E \rangle = \text{const.}$

$$S_E(\omega) = \frac{1}{\pi} \int_0^\infty \Delta^2 \frac{\Gamma_\uparrow \Gamma_\downarrow}{\Gamma_\Sigma^2} e^{-\Gamma_\Sigma \tau} \cos \omega \tau d\tau = \frac{\Delta^2}{\pi \Gamma_\Sigma} \frac{\Gamma_\uparrow \Gamma_\downarrow}{\Gamma_\Sigma^2 + \omega^2}. \quad (5.177)$$

Such dependence on frequency⁶⁶ is very typical for discrete-state systems described by master equations. It is interesting that the most widely accepted explanation of the $1/f$ noise (also called the “flicker” or “excess” noise), which was mentioned in Sec. 5, is that it is a result of thermally-activated jumps between metastable states of a statistical ensemble of such two-level systems, with an exponentially-broad statistical distribution of transition rates $\Gamma_{\uparrow,\downarrow}$. Such a broad distribution follows from the Kramers formula (156), which is approximately valid for lifetimes of states of systems with double-well potential profiles (Fig. 13), for a statistical ensemble with a smooth statistical distribution of energy gaps Δ . Such profiles are typical, in particular, for electrons in disordered (amorphous) solid-state materials that, indeed, feature high $1/f$ noise.

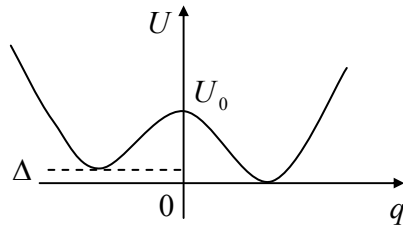


Fig. 5.13. Typical double-well potential profile.

Returning to the Fokker-Planck equation, we may use the evident generalization of Eq. (168) to the continuous-variable case:

$$\langle f(t)f(t+\tau) \rangle = \int d^3 q d^3 p \int d^3 q' d^3 p' f(\mathbf{q}, \mathbf{p}) w(\mathbf{q}, \mathbf{p}, \infty) f(\mathbf{q}', \mathbf{p}') w(\mathbf{q}', \mathbf{p}', \tau), \quad (5.178)$$

Correlation
function of
continuous-
state
system

were both probability density distributions are solutions of the equation with the delta-functional initial condition

$$w(\mathbf{q}', \mathbf{p}', 0) = \delta(\mathbf{q}' - \mathbf{q}) \delta(\mathbf{p}' - \mathbf{p}). \quad (5.179)$$

For the Smoluchowski equation, valid in the high-damping limit, the expressions are similar, albeit with a lower dimensionality:

$$\langle f(t)f(t+\tau) \rangle = \int d^3 q \int d^3 q' f(\mathbf{q}) w(\mathbf{q}, \infty) f(\mathbf{q}') w(\mathbf{q}', \tau), \quad (5.180)$$

$$w(\mathbf{q}', 0) = \delta(\mathbf{q}' - \mathbf{q}). \quad (5.181)$$

To see this formalism in action, let us use it to find the correlation function $K_q(\tau)$ of a *linear relaxator*, i.e. an overdamped 1D harmonic oscillator with $m\omega_0 \ll \eta$. In this limit, the coordinate averaged over the heat baths obeys a linear equation,

$$\eta \langle \dot{q} \rangle + \kappa \langle q \rangle = 0, \quad (5.182)$$

which describes its exponential relaxation from a certain initial condition q_0 to the equilibrium position $q = 0$, with the reciprocal time constant $\Gamma = \kappa/\eta$:

⁶⁶ Regardless of the physical sense of such function of ω , and of whether its maximum is situated at either zero as in Eq. (177), or at a finite frequency ω_0 as in Eq. (68), it is often referred to as the *Lorentzian* (or “Breit-Wigner”) line.

$$\langle q \rangle(t) = q_0 e^{-\Gamma t}. \quad (5.183)$$

The deterministic equation (182) corresponds to the quadratic potential energy $U(q) = \kappa q^2/2$, so that the 1D version of the Smoluchowski equation (122) takes the following form:

$$\eta \frac{\partial w}{\partial t} = \kappa \frac{\partial}{\partial q} (wq) + T \frac{\partial^2 w}{\partial q^2}. \quad (5.184)$$

It is straightforward to check, by substitution, that this equation, rewritten for function $w(q', \tau)$, with the delta-functional initial condition (181), $w(q', 0) = \delta(q' - q)$, is satisfied by a Gaussian function,

$$w(q', \tau) = \frac{1}{(2\pi)^{1/2} \delta q(\tau)} \exp \left\{ -\frac{(q' - \langle q \rangle(\tau))^2}{2\delta q^2(\tau)} \right\}, \quad (5.185)$$

with its center, $\langle q \rangle(\tau)$, moving in accordance with Eq. (183), and the time-dependent variance

$$\delta q^2(\tau) = \delta q^2(\infty) (1 - e^{-2\Gamma \tau}) \quad \text{where} \quad \delta q^2(\infty) = \langle q^2 \rangle = \frac{T}{\kappa}. \quad (5.186)$$

(As a sanity check, the last equality coincides with the equipartition theorem's result.) Finally, the first probability under the integral in Eq. (180) may be found from Eq. (185) in the limit $\tau \rightarrow \infty$ (in which $\langle q \rangle(\tau) \rightarrow 0$), by replacing q' for q :

$$w(q, \infty) = \frac{1}{(2\pi)^{1/2} \delta q(\infty)} \exp \left\{ -\frac{q^2}{2\delta q^2(\infty)} \right\}. \quad (5.187)$$

Now, all components of recipe (180) are ready, and we can write it, for $f(q) = q$, as

$$\langle q(t)q(t+\tau) \rangle = \frac{1}{2\pi \delta q(\tau) \delta q(\infty)} \int_{-\infty}^{+\infty} dq' \int_{-\infty}^{+\infty} dq \exp \left\{ -\frac{q^2}{2\delta q^2(\infty)} \right\} q' \exp \left\{ -\frac{(q' - qe^{-\Gamma \tau})^2}{2\delta q^2(\tau)} \right\}. \quad (5.188)$$

The integral over q' may be worked out first, by the replacing that integration variable with $(q'' + qe^{-\Gamma \tau})$ and hence dq' with dq'' :

$$\langle q(t)q(t+\tau) \rangle = \frac{1}{2\pi \delta q(\tau) \delta q(\infty)} \int_{-\infty}^{+\infty} q \exp \left\{ -\frac{q^2}{2\delta q^2(\infty)} \right\} dq \int_{-\infty}^{+\infty} (q'' + qe^{-\Gamma \tau}) \exp \left\{ -\frac{q''^2}{2\delta q^2(\tau)} \right\} dq''. \quad (5.189)$$

The integral of the first term in parentheses ($q'' + qe^{-\Gamma \tau}$) equals zero (as that of an odd function in symmetric integration limits), while that with the second term is the standard Gaussian integral, giving

$$\langle q(t)q(t+\tau) \rangle = \frac{1}{(2\pi)^{1/2} \delta q(\infty)} e^{-\Gamma \tau} \int_{-\infty}^{+\infty} q^2 \exp \left\{ -\frac{q^2}{2\delta q^2(\infty)} \right\} dq = \frac{2T}{\pi^{1/2} \kappa} e^{-\Gamma \tau} \int_{-\infty}^{+\infty} \xi^2 \exp \{-\xi^2\} d\xi. \quad (5.190)$$

The last integral⁶⁷ is just $\pi^{1/2}/2$, so that taking into account that for this stationary system centered at the coordinate origin, the ensemble average $\langle q \rangle = 0$,⁶⁸ we finally get a very simple result,

⁶⁷ See, e.g., MA Eq. (6.9c).

$$K_q(\tau) \equiv \langle \tilde{q}(t) \tilde{q}(t+\tau) \rangle = \langle q(t) q(t+\tau) \rangle - \langle q \rangle^2 = \langle q(t) q(t+\tau) \rangle = \frac{T}{\kappa} e^{-\Gamma \tau}. \quad (5.191)$$

As a sanity check, for $\tau = 0$ it yields $K_q(0) \equiv \langle q^2 \rangle = T/\kappa$, in accordance with Eq. (186). As τ is increased the correlation function decreases monotonically – see the solid-line sketch in Fig. 8.

So, the solution of this very simple problem has required straightforward but somewhat bulky calculations. On the other hand, the same result may be obtained literally in one line, using the Langevin formalism – namely, as the Fourier transform (59) of the spectral density (68) in the corresponding limit $m\omega \ll \eta$, with $S_A(\omega)$ given by Eq. (73):⁶⁹

$$K_q(\tau) = 2 \int_0^\infty S_q(\omega) \cos \omega \tau \, d\omega = 2 \int_0^\infty \frac{\eta T}{\pi} \frac{1}{\kappa^2 + (\eta \omega)^2} \cos \omega \tau \, d\omega = 2 \frac{T\Gamma}{\pi} \int_0^\infty \frac{\cos \xi}{(\Gamma \tau)^2 + \xi^2} \, d\xi = \frac{T}{\kappa} e^{-\Gamma \tau}. \quad (5.192)$$

This example illustrates well that for linear systems (and small fluctuations in nonlinear systems) the Langevin approach is usually much simpler than the one based on the Fokker-Planck or Smoluchowski equations. However, again, the latter approach is indispensable for the analysis of fluctuations of arbitrary intensity in nonlinear systems.

To conclude this chapter, I have to emphasize again that the Fokker-Planck and Smoluchowski equations give a quantitative description of time evolution of nonlinear Brownian systems with finite dissipation in the *classical* limit. The description of quantum properties of such dissipative (“open”) and nonlinear *quantum* systems is more complex,⁷⁰ and only a few simple problems of such theory have been solved so far,⁷¹ typically using a particular model of the environment, e.g., as a large set of harmonic oscillators with different statistical distributions of their parameters, leading to different frequency dependence of susceptibility $\chi(\omega)$.

5.10. Exercise problems

5.1. Considering the first 30 digits of number $\pi = 3.1415\dots$ as a statistical ensemble of integers k (equal to 3, 1, 4, 1, 5, ...), calculate

- (i) average $\langle k \rangle$, and
- (ii) the r.m.s. fluctuation δk .

Compare the results with those for an ensemble of completely random integers 0, 1, ..., 9, and comment.

5.2. For a set of N non-interacting Ising “spins” $s_j = \pm 1$, placed into magnetic field h , calculate the relative fluctuation of system’s magnetization.

Hint: The total magnetic moment of an Ising system is assumed to be proportional to the sum

⁶⁸ This fact is not in any contradiction with the nonvanishing result (183) which is only valid for a sub-ensemble with a certain (deterministic) initial condition q_0 .

⁶⁹ The involved table integral may be found, e.g., in MA Eq. (6.11).

⁷⁰ See, e.g., QM Sec. 7.6.

⁷¹ See, e.g., the solutions of the 1D Kramers problem for quantum systems with low damping by A. Caldeira and A. Leggett, *Phys. Rev. Lett.* **46**, 211 (1981), and with high damping by A. Larkin and Yu. Ovchinnikov, *JETP Lett.* **37**, 382 (1983).

$$\mathcal{S} \equiv \sum_{j=1}^N s_j ,$$

so that the requested relative fluctuation may be calculated just as $\delta\mathcal{S}/\langle\mathcal{S}\rangle$.

5.3. For a field-free, two-site Ising system with energy values $E_m = -Js_1s_2$, in the thermal equilibrium at temperature T , find the variance of energy fluctuations. Explore the low-temperature and high-temperature limits of the result.

5.4. For the 1D, three-site Ising ring with ferromagnetic coupling (and no external field), calculate the correlation coefficient $\langle s_j s_{j'} \rangle$ for both $j = j'$ and $j \neq j'$.

5.5. Within the framework of Weiss' molecular-field theory, calculate the variance of spin fluctuations in the d -dimensional Ising model. Use the result to derive the conditions of quantitative validity of the theory.

5.6. Calculate the variance of fluctuations of the energy of a quantum harmonic oscillator of frequency ω , in thermal equilibrium at temperature T , and express it via the average value of the energy.

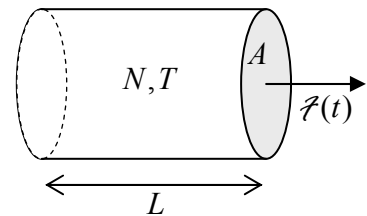
5.7. Express the r.m.s. fluctuation of the occupancy N_k of a certain energy level ε_k by:

- (i) a classical particle,
- (ii) a fermion, and
- (iii) a boson,

in the thermodynamic equilibrium, via the average occupancy $\langle N_k \rangle$, and compare the results.

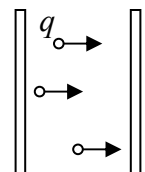
5.8.* Starting from the Maxwell distribution of velocities, calculate constant C in the (approximate) expression $K_P(\tau) = C\delta(\tau)$, for the correlation function of fluctuations of pressure $P(t)$ of an ideal gas of N classical particles. Compare the result with that of Problem 3.2, and estimate the pressure fluctuation variance.

Hint: You may like to consider a cylindrically-shaped container of volume $V = LA$ (see Fig. on the right) to calculate fluctuations of force acting on its plane lid of area A , and then recalculate them into fluctuations of pressure P .



5.9. Perhaps the simplest model of diffusion is the 1D *discrete random walk*: each time interval τ , a particle leaps, with equal probability, to any of two neighboring sites of a 1D lattice with the spatial period a . Prove that particle's displacement during time interval $t \gg \tau$, obeys Eq. (77), and calculate the corresponding diffusion coefficient D .

5.10.* Calculate the low-frequency spectral density of current $I(t)$ due to random passage of charged particles between two conducting electrodes - see Fig. on the right. Assume that the particles are emitted by one of the electrodes at random times, and are fully absorbed by the counterpart electrode.



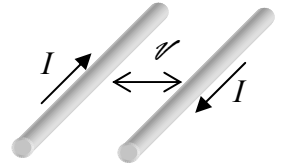
5.11.* Within the rotating-wave approximation (RWA),⁷² calculate major statistical properties of fluctuations of the phase of classical self-oscillations, at:

- (i) the free run of the oscillator, and
- (ii) its phase locking by an external sinusoidal force,

assuming that the fluctuations are caused by a weak, broadband noise with spectral density $S_f(\omega)$.

5.12. Calculate the correlation function of the coordinate of a 1D harmonic oscillator with small Ohmic damping at thermal equilibrium.

5.13. Consider a very long, uniform, two-wire transmission line (see Fig. on the right), that allows the propagation of TEM waves with negligible attenuation, in thermal equilibrium with the environment at temperature T . Find variance $\langle \mathcal{V}^2 \rangle_{\Delta\nu}$ of electromagnetic fluctuations of voltage $\mathcal{V}$ between the wires within a small frequency interval $\Delta\nu$.

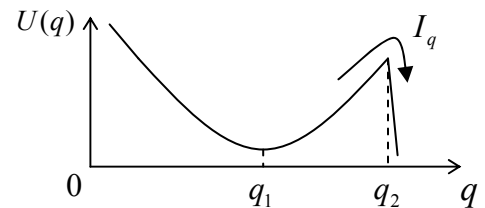


Hint: As an E&M reminder,⁷³ TEM waves propagate with a frequency-independent velocity (equal to c if the wires are in vacuum), with voltage $\mathcal{V}$ and current I (see Fig. above) related as $\mathcal{V}(x,t)/I(x,t) = \pm \mathcal{Z}$, where $\mathcal{Z}$ is a frequency-independent constant (“wave impedance”).

5.14. Now consider a similar line terminated, at one end, with an impedance-matching resistor $R = \mathcal{Z}$. Find variance $\langle \mathcal{V}^2 \rangle_{\Delta\nu}$ of the voltage across the resistor, and discuss the relation between the result and the Nyquist theorem (81).

Hint: Take into account that resistor with $R = \mathcal{Z}$ absorbs incident TEM waves without reflection.

5.15. An overdamped classical 1D particle escapes from a potential well with a smooth bottom, but a sharp edge – see Fig. on the right. Find the appropriate modification of the Kramers formula (139).



5.16. A particle may occupy any of N similar sites. Particle’s interaction with environment induces its random, incoherent jumps from the occupied site to any other one with the same rate Γ . Find the correlation function and the spectral density of fluctuations of the instant occupancy $n(t)$ (equal to either 1 or 0) of any particular site.

⁷² See, e.g., CM Sec. 4.3.

⁷³ See, e.g., EM Sec. 7.6.

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Chapter 6. Elements of Kinetics

This chapter gives a brief introduction to the basic notions of physical kinetics. Its main focus is on the Boltzmann equation, especially within the relaxation-time approximation, which allows, in particular, an approximate but reasonable and simple description of transport phenomena (such as the electric current and thermoelectric effects) in gases, including electron gases in metals and semiconductors.

6.1. The Liouville theorem

Physical kinetics is the branch of statistical physics that deals with systems out of thermodynamic equilibrium. Major tasks of kinetics include:

- (i) for *autonomous* systems (those out of external fields): transient processes (*relaxation*) leading from an arbitrary initial state of a system to the thermodynamic equilibrium;
- (ii) for systems in time-dependent external fields (say, in a sinusoidal “ac” field): the periodic oscillations of system’s parameters; and
- (iii) for systems in time-independent (“dc”) external fields: dc transport effects.

In the last case, we are dealing with stationary ($\partial/\partial t = 0$ everywhere), but *non-equilibrium* situations, in which the effect of an external field, continuously driving the system out of the equilibrium, is balanced by the simultaneous relaxation – the trend toward the equilibrium. Perhaps the most important effect of this class is the dc current in conductors, which alone justifies the inclusion of the basic notions of kinetics into any set of core physics courses.

Actually, the reader who has reached this point of the notes, already has a good taste of physical kinetics, because the subject of the last part of Chapter 5 *was* the kinetics of a “Brownian particle”, i.e. of a “heavy” system interacting with environment consisting of many “lighter” components. Indeed, the equations discussed in that part - whether the Smoluchowski equation (5.122) or the Fokker-Planck equation (5.149) - are valid if the environment is in thermodynamic equilibrium, but the system of our interest is not necessarily so. As a result, we could use those equations to discuss such non-equilibrium phenomena as the Kramers problem for the metastable state lifetime.

This chapter is devoted to the more traditional subject of kinetics: a system of very many *similar* particles – generally, interacting with each other, but not too strongly, so that the energy of the system still may be partitioned into a sum of the components, with the component interactions considered as a weak perturbation. Actually, we have already started the job of describing such a system in Sec. 5.8, in the course of deriving the Fokker-Planck equation for a single classical particle. Indeed, in the absence of particle interactions (i.e. when it is unimportant whether the particle is light or heavy), the probability current densities in the coordinate and momentum spaces are given, respectively, by Eqs. (5.142) and (5.143), so that the continuity equation (5.140) takes the form

$$\frac{\partial w}{\partial t} + \nabla_q \cdot (w \dot{\mathbf{q}}) + \nabla_p \cdot (w \dot{\mathbf{p}}) = 0. \quad (6.1)$$

If similar particles do *not* interact, this equation for single-particle probability density $w(\mathbf{q}, \mathbf{p}, t)$ is valid for each of them, and the result of its solution may be used to calculate any average of the system as a whole.

Let us rewrite Eq. (1) in the Cartesian component form,

$$\frac{\partial w}{\partial t} + \sum_j \left[\frac{\partial}{\partial q_j} (w \dot{q}_j) + \frac{\partial}{\partial p_j} (w \dot{p}_j) \right] = 0, \quad (6.2)$$

where index j lists all degrees of freedom of the particle, and assume that its motion in an external field may be described by a Hamiltonian function $\mathcal{H}(q_j, p_j, t)$. Plugging into Eq. (2) the Hamiltonian equations of motion:¹

$$\dot{q}_j = \frac{\partial \mathcal{H}}{\partial p_j}, \quad \dot{p}_j = -\frac{\partial \mathcal{H}}{\partial q_j}, \quad (6.3)$$

we get

$$\frac{\partial w}{\partial t} + \sum_j \left[\frac{\partial}{\partial q_j} \left(w \frac{\partial \mathcal{H}}{\partial p_j} \right) - \frac{\partial}{\partial p_j} \left(w \frac{\partial \mathcal{H}}{\partial q_j} \right) \right] = 0. \quad (6.4)$$

At the parentheses' differentiation, the mixed terms $w \partial^2 \mathcal{H} / \partial q_j \partial p_j$ and $w \partial^2 \mathcal{H} / \partial p_j \partial q_j$ cancel, and using Eq. (3) again, we get the so-called *Liouville theorem*²

$$\boxed{\frac{\partial w}{\partial t} + \sum_j \left(\frac{\partial w}{\partial q_j} \dot{q}_j + \frac{\partial w}{\partial p_j} \dot{p}_j \right)} = 0. \quad (6.5) \quad \text{Liouville theorem}$$

Since the left-hand part of this equation is just the full derivative of the probability density considered as a function of the generalized coordinates $q_j(t)$ of a particle, its generalized momenta components $p_j(t)$, and (possibly) time t , the Liouville theorem (5) may be presented in a surprisingly simple form:

$$\frac{dw(\mathbf{q}, \mathbf{p}, t)}{dt} = 0. \quad (6.6)$$

Physically it means that the probability $dW = w d^3 q d^3 p$ to find a Hamiltonian particle in a small volume of the coordinate-momentum space $[\mathbf{q}, \mathbf{p}]$, with the center moving in accordance to the deterministic law (3), does not change with time – see Fig. 1.

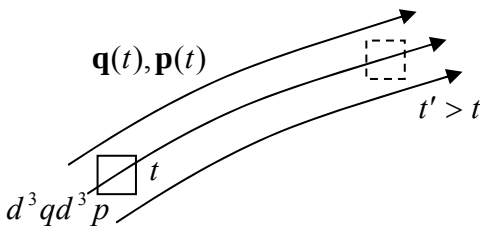


Fig. 6.1. Cartoon representation of the Liouville theorem in the 6D space $[\mathbf{q}, \mathbf{p}]$.

¹ See, e.g., CM Sec. 10.1.

² Actually, this is just one of several theorems bearing the name of J. Liouville (1809-1882).

At the first glance, this may not look surprising, because according to the fundamental Einstein relation (5.78), one needs non-Hamiltonian forces (such as viscosity) to have diffusion. On the other hand, it is striking that the Liouville theorem is valid even for (Hamiltonian) systems with deterministic chaos,³ in which the deterministic trajectories corresponding to slightly different initial conditions become increasingly mixed with time.

For an ideal gas of 3D particles, we may select the usual Cartesian coordinates r_j (with $j = 1, 2, 3$) for the generalized coordinates q_j , so that p_j become the Cartesian components mv_j of the usual (linear) momentum, and the elementary volume is just $d^3r d^3p$ – see Fig. 1. In this case Eqs. (3) are just

$$\dot{r}_j = \frac{p_j}{m} \equiv v_j, \quad \dot{p}_j = \mathcal{F}_j, \quad (6.7)$$

so that the Liouville theorem may be rewritten as

$$\frac{\partial w}{\partial t} + \sum_{j=1}^3 \left(v_j \frac{\partial w}{\partial r_j} + \mathcal{F}_j \frac{\partial w}{\partial p_j} \right) = 0, \quad (6.8)$$

and conveniently presented in the vector form⁴

$$\frac{\partial w}{\partial t} + \mathbf{v} \cdot \nabla w + \boldsymbol{\mathcal{F}} \cdot \nabla_p w = 0, \quad (6.9)$$

where I have returned to using unindexed symbol ∇ for the vector differentiation in the coordinate space.

6.2. The Boltzmann equation

The situation becomes much more complex if particles interact. Generally, a system of N similar particles in 3D space has to be described by probability density w being a function of $6N + 1$ arguments ($3N$ Cartesian coordinates, plus $3N$ momentum components, plus time). Analytical or numerical solution of any equation describing time evolution of such a function for a typical ensemble of $N \sim 10^{23}$ particles is evidently a hopeless task. Hence, kinetics of realistic ensembles has to rely on making reasonable approximations with simplify the situation.

One of the most useful approximation (sometimes called *Stosszahlansatz*, German for the “collision number assumption”) was suggested by L. Boltzmann for a gas of particles that move freely most of the time, but interact during short time intervals, when a particle comes close to either an immobile scattering center (say, an impurity in a conductor) or to another particle of the gas. Such a brief *scattering event* changes particle’s momentum, and may be approximately described by the addition of a special term (called the *scattering integral*) to the right-hand part of Eq. (9):

$$\frac{\partial w}{\partial t} + \mathbf{v} \cdot \nabla w + \boldsymbol{\mathcal{F}} \cdot \nabla_p w = \frac{\partial w}{\partial t} \Big|_{\text{scattering}}, \quad (6.10)$$

while still keeping w a function of only 7 arguments: 3 coordinate components of vector $\mathbf{r}$ and 3 components of momentum $\mathbf{p}$ (all of just one particle), plus time t . This is the *Boltzmann transport equation*.

³ See, e.g., CM Sec. 9.3.

⁴ From this point on, I return to using the index-free symbol

The concrete form of the scattering integral depends on the scattering object. If scattering centers do not belong to the ensemble under consideration (again, for example, an impurity atom in a conductor – see Fig. 2), then the scattering integral may be obtained by an evident generalization of the master equation (4.100):⁵

$$\left. \frac{\partial w}{\partial t} \right|_{\text{scattering}} = \int d^3 p' \left[\Gamma_{\mathbf{p}' \rightarrow \mathbf{p}} w(\mathbf{r}, \mathbf{p}', t) - \Gamma_{\mathbf{p} \rightarrow \mathbf{p}'} w(\mathbf{r}, \mathbf{p}, t) \right], \quad (6.11)$$

where the physical sense of $\Gamma_{\mathbf{p} \rightarrow \mathbf{p}'}$ is the rate (i.e. the probability per unit time) for the particle to be scattered from the state with momentum $\mathbf{p}$ into the state with momentum $\mathbf{p}'$.

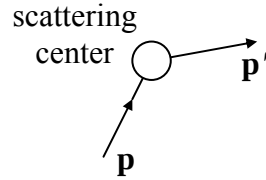


Fig. 6.2. Particle scattering event.

Most elastic interactions are *reciprocal*, i.e. obey the following relation (closely related to the reversibility of time in Hamiltonian systems): $\Gamma_{\mathbf{p} \rightarrow \mathbf{p}'} = \Gamma_{\mathbf{p}' \rightarrow \mathbf{p}}$, so that Eq. (11) may be rewritten as⁶

$$\left. \frac{\partial w}{\partial t} \right|_{\text{scattering}} = \int d^3 p' \Gamma_{\mathbf{p} \rightarrow \mathbf{p}'} [w(\mathbf{r}, \mathbf{p}', t) - w(\mathbf{r}, \mathbf{p}, t)]. \quad (6.12)$$

With such scattering integral, Eq. (10) stays linear in w , but becomes an *integro-differential equation*, typically harder to solve than differential equations.

The equation becomes even more complex if the scattering is due to mutual interaction of the particle members of the system (Fig. 3).

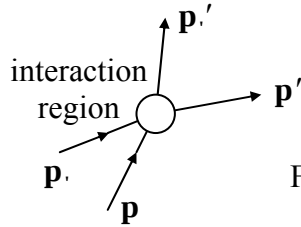


Fig. 6.3. Particle-particle scattering event.

⁵ Note that the master equations ignores possible quantum coherence of different scattering events, described by off-diagonal elements of the density matrix, because w represents only the diagonal elements of the matrix. However, for ensembles close to thermal equilibrium, this is a reasonable approximation – see Sec. 2.1.

⁶ One may wonder whether this approximation may work for Fermi particles, for whom the Pauli principle forbids scattering into the already occupied state, so that for scattering $\mathbf{p} \rightarrow \mathbf{p}'$, factor $w(\mathbf{r}, \mathbf{p}, t)$ in Eq. (12) has to be multiplied by the probability $[1 - w(\mathbf{r}, \mathbf{p}', t)]$ that the final state is available. Generally, this is a valid argument, but one should notice that if this modification has been done with both terms of Eq. (12), it yields

$$\left. \frac{\partial w}{\partial t} \right|_{\text{scattering}} = \int d^3 p' \Gamma_{\mathbf{p} \rightarrow \mathbf{p}'} \left\{ w(\mathbf{r}, \mathbf{p}', t) [1 - w(\mathbf{r}, \mathbf{p}, t)] - w(\mathbf{r}, \mathbf{p}, t) [1 - w(\mathbf{r}, \mathbf{p}', t)] \right\}.$$

Opening both square brackets, we see that the probability density products cancel, bringing us back to Eq. (12).

In this case, the probability of the scattering event scales as a product of two single-particle probabilities, and the simplest form of the scattering integral is⁷

$$\left. \frac{\partial w}{\partial t} \right|_{\text{scattering}} = \int d^3 p' \int d^3 p \left[\Gamma_{\mathbf{p}' \rightarrow \mathbf{p}, \mathbf{p}' \rightarrow \mathbf{p}} w(\mathbf{r}, \mathbf{p}', t) w(\mathbf{r}, \mathbf{p}', t) - \Gamma_{\mathbf{p} \rightarrow \mathbf{p}', \mathbf{p} \rightarrow \mathbf{p}'} w(\mathbf{r}, \mathbf{p}, t) w(\mathbf{r}, \mathbf{p}, t) \right]. \quad (6.13)$$

The integration dimensionality in Eq. (13) takes into account the fact that due to the conservation of the total momentum at scattering,

$$\mathbf{p} + \mathbf{p}' = \mathbf{p}' + \mathbf{p}', \quad (6.14)$$

one of the momenta is not an independent argument, so that the integration in Eq. (13) may be restricted to a 6D p -space rather than the 9D one. For the reciprocal interaction, Eq. (13) may also be a bit simplified, but it still keeps Eq. (10) a *nonlinear* integro-differential transport equation, excluding such powerful solution methods as the Fourier expansion (which hinges on the linear superposition principle).

This is why most useful results based on the Boltzmann transport equation hinge on its further simplifications, most notably the *relaxation-time approximation* – RTA for short.⁸ This approximation is based on noticing that in the absence of spatial gradients ($\nabla = 0$), and external forces ($\mathcal{F} = 0$), Eq. (10) yields

$$\left. \frac{\partial w}{\partial t} \right|_{\text{scattering}} = \left. \frac{\partial w}{\partial t} \right|_{\text{scattering}}, \quad (6.15)$$

so that the thermally-equilibrium probability distribution $w_0(\mathbf{r}, \mathbf{p}, t)$ has to turn any scattering integral into zero. Hence at *small* deviations from the equilibrium,

$$\tilde{w}(\mathbf{r}, \mathbf{p}, t) \equiv w(\mathbf{r}, \mathbf{p}, t) - w_0(\mathbf{r}, \mathbf{p}, t) \rightarrow 0, \quad (6.16)$$

the scattering integral should be proportional to the deviation $\tilde{w}$, and its simplest reasonable model is

Relaxation-
time
approximation
(RTA)

$$\left. \frac{\partial w}{\partial t} \right|_{\text{scattering}} = -\frac{\tilde{w}}{\tau}, \quad (6.17)$$

where τ is a phenomenological constant (which, according to Eq. (15), has to be positive for system's stability) called the *relaxation time*. Its physical meaning will be more clear in the next section.

The relaxation-time approximation is quite reasonable if the angular distribution of the scattering rate is dominated by small angles between vectors $\mathbf{p}$ and $\mathbf{p}'$ – as it is, for example, for the Rutherford scattering by a Coulomb center.⁹ Indeed, in this case the two functions w , participating in Eq. (12) are close to each other, so that the loss of the second momentum argument ($\mathbf{p}'$) is not too essential. However, while using the Boltzmann-RTA equation, which results from combining Eqs. (10) and (17),

Boltzmann-
RTA
equation

$$\left. \frac{\partial w}{\partial t} \right|_{\text{scattering}} + \mathbf{v} \cdot \nabla w + \mathcal{F} \cdot \nabla_p w = -\frac{\tilde{w}}{\tau}, \quad (6.18)$$

⁷ This was the approximation used by L. Boltzmann to prove the famous *H-theorem*, stating that entropy of the gas described by Eq. (13) may only grow (or stay constant) in time, $dS/dt \geq 0$. Since the model is very approximate, that result does not seem too fundamental nowadays, despite all its historic significance.

⁸ Sometimes this approximation is called the “BGK model”, after P. Bhatnager, E. Gross, and M. Krook who suggested it in 1954. (The same year, a similar model was considered by P. Welander.)

⁹ See, e.g., CM Sec. 3.7.

the reader should always remember this is just an approximation, sometimes giving completely wrong results. For example, it prescribes the same time scale, τ , to the relaxation of the net *momentum* of the system, and to its *energy* relaxation, while in many real systems the latter process (that requires inelastic interactions) may be substantially longer. Naturally, in the following sections I will describe only those applications of the RTA approximation that give a reasonable description of reality.

6.3. The Ohm law and the Drude formula

Despite its shortcomings, Eq. (18) is adequate for quite a few applications. Perhaps the most important of them is deriving the Ohm law for dc current in a gas of charged particles, whose only important deviation from ideality is the scattering in the form of Eq. (17), and hence described, in equilibrium, by the equilibrium probability w_0 of an ideal gas (see Sec. 3.1):

$$w_0(\mathbf{r}, \mathbf{p}, t) = \frac{g}{(2\pi\hbar)^3} \langle N(\varepsilon) \rangle, \quad (6.19)$$

where g is the degeneracy factor (say, $g = 2$ for electrons due to their spin), and $\langle N(\varepsilon) \rangle$ is the average occupancy of a quantum state with momentum $\mathbf{p}$, that obeys either the Fermi-Dirac or the Bose-Einstein distribution:

$$\langle N(\varepsilon) \rangle = \frac{1}{e^{(\varepsilon - \mu)/T} \pm 1}, \quad \varepsilon = \varepsilon(\mathbf{p}). \quad (6.20)$$

(Up to a point, our calculations will be valid for both statistics, and hence, in the limit $\mu/T \rightarrow -\infty$, for a classical gas as well.)

Now let a uniform, dc electric field $\mathcal{E}$ be applied to the gas, exerting force $\mathcal{F} = q\mathcal{E}$ on each particle with electric charge q . Then the stationary solution to Eq. (18), with $\partial/\partial t = 0$, should also be stationary and spatially-uniform ($\nabla = 0$), so that this equation is reduced to

$$q\mathcal{E} \cdot \nabla_p w = -\frac{\tilde{w}}{\tau}. \quad (6.21)$$

Let us assume the electric field to be relatively low as well, so that the perturbation $\tilde{w}$ it produces is relatively small. (I will quantify this condition later on.) Then in the left-hand side of Eq. (21) we can neglect that perturbation, by replacing w with w_0 , because that side already has a small factor ($\mathcal{E}$). As a result, this equation yields

$$\tilde{w} = -\tau q\mathcal{E} \cdot \nabla_p w_0 = -\tau q\mathcal{E} \cdot \left(\nabla_p \varepsilon \right) \frac{\partial w_0}{\partial \varepsilon}, \quad (6.22)$$

where the partial derivative sign marks the implied local constancy of parameters μ and T , i.e. their independence of momentum $\mathbf{p}$. But gradient $\nabla_p \varepsilon$ is nothing else than particle's velocity $\mathbf{v}$ - for a quantum particle, its group velocity.¹⁰ (This fact is easy to verify for the isotropic and parabolic dispersion law, pertinent to classical particles moving in free space,

¹⁰ See, e.g., QM Sec. 2.1.

$$\varepsilon(\mathbf{p}) = \frac{p^2}{2m} = \frac{p_1^2 + p_2^2 + p_3^2}{2m}. \quad (6.23)$$

Indeed, in this case the Cartesian components of vector $\nabla_p \varepsilon$ are

$$(\nabla_p \varepsilon)_j \equiv \frac{\partial \varepsilon}{\partial p_j} = \frac{p_j}{m} = v_j, \quad (6.24)$$

so that $\nabla_p \varepsilon = \mathbf{v}$.) Hence, Eq. (22) may be rewritten as

$$\tilde{w} = -\tau q \boldsymbol{\mathcal{E}} \cdot \mathbf{v} \frac{\partial w_0}{\partial \varepsilon}. \quad (6.25)$$

Let us use this result to calculate the electric current density $\mathbf{j}$. The contribution of each quantum state to the current density is $q\mathbf{v}w$, so that the total density is

$$\mathbf{j} = \int q\mathbf{v}w d^3 p = q \int \mathbf{v}(w_0 + \tilde{w}) d^3 p. \quad (6.26)$$

Since in the equilibrium state (with $w = w_0$), the current has to be zero, integral of the first term in the parentheses has to vanish. For the integral of the second term, plugging in Eq. (25), and also using Eq. (19), we get

Sommerfeld
theory's
result

$$\mathbf{j} = q^2 \tau \int \mathbf{v}(\boldsymbol{\mathcal{E}} \cdot \mathbf{v}) \left(-\frac{\partial w_0}{\partial \varepsilon} \right) d^3 p = \frac{g q^2 \tau}{(2\pi\hbar)^3} \int \mathbf{v}(\boldsymbol{\mathcal{E}} \cdot \mathbf{v}) \left(-\frac{\partial \langle N(\varepsilon) \rangle}{\partial \varepsilon} \right) d^2 p_{\perp} dp_{||}, \quad (6.27)$$

where $d^2 p_{\perp}$ is the elementary area of the constant energy surface in the momentum space, while $dp_{||}$ is the momentum differential's component normal to that surface. This result¹¹ is valid even for particles with an arbitrary dispersion law $\varepsilon(\mathbf{p})$ (that may be rather complicated, for example, for particles moving in space-periodic potentials¹²), and may give, in particular, a fair description of conductivity's anisotropy in crystals.

For classical particles whose dispersion law is isotropic and parabolic, as in Eq. (23), the constant energy surface is a sphere of radius p , so that $d^2 p_{\perp} = p^2 d\Omega = p^2 \sin\theta d\theta d\varphi$, while $dp_{||} = dp$. In spherical coordinates with the polar axis direction along vector $\boldsymbol{\mathcal{E}}$, we get $(\boldsymbol{\mathcal{E}} \cdot \mathbf{v}) = \mathcal{E} v \cos\theta$. Now separating vector $\mathbf{v}$ outside the parentheses into a component $v \cos\theta$ directed along vector $\boldsymbol{\mathcal{E}}$, and two perpendicular components, $v \sin\theta \cos\varphi$ and $v \sin\theta \sin\varphi$, we see that the integrals of the last two components over angle φ give zero. Hence, as we could expect, in the isotropic case the net current is directed along the electric field and obeys the linear *Ohm law*,¹³

$$\mathbf{j} = \sigma \boldsymbol{\mathcal{E}}, \quad (6.28)$$

with a field-independent *electric conductivity*

¹¹ First obtained by A. Sommerfeld in 1927.

¹² See, e.g., QM Secs. 2.7, 2.8, and 3.4. In this case, $\mathbf{p}$ should be understood as the quasi-momentum rather than genuine momentum.

¹³ As Eq. (27) shows, if the dispersion law $\varepsilon(\mathbf{p})$ is anisotropic, the direction of current density may be different from that of the electric field. In this case, conductivity should be described by a tensor σ_{ij} , rather than a scalar.

$$\sigma = \frac{gq^2\tau}{(2\pi\hbar)^3} \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta \cos^2\theta \int_0^\infty p^2 dp v^2 \left(-\frac{\partial \langle N(\varepsilon) \rangle}{\partial \varepsilon} \right). \quad (6.29)$$

Since $\sin\theta d\theta$ is just $-d(\cos\theta)$, the integral over θ equals $(2/3)$. The integral over $d\varphi$ is of course just 2π , while that over p may be readily transformed to one over particle's energy $\varepsilon(\mathbf{p}) = p^2/2m$: $vd\mathbf{p} = pdp/m = d\varepsilon$, so that $p^2 dp v^2 = p^2 v d\varepsilon = (2m\varepsilon)(2\varepsilon/m)^{1/2} d\varepsilon = (8m\varepsilon^3)^{1/2} d\varepsilon$. As a result, the conductivity equals

$$\sigma = \frac{gq^2\tau}{(2\pi\hbar)^3} \frac{4\pi}{3} \int_0^\infty (8m\varepsilon^3)^{1/2} \left(-\frac{\partial \langle N(\varepsilon) \rangle}{\partial \varepsilon} \right) d\varepsilon. \quad (6.30)$$

Note that σ is proportional to q^2 and hence does not depend on the particle charge sign; this is why the Hall effect in external magnetic field, which lacks this ambivalence, is typically used to determine the charge of current carriers (electrons or holes) in semiconductors.

So far, the calculations have been valid for any gas (Bose, Fermi, or classical), an arbitrary temperature. Let us work out the remaining integral over energy for the most important case of a degenerate Fermi (say, electron) gas, with $T \ll \varepsilon_F$.¹⁴ As was discussed in Sec. 3.3, in this limit, factor $(-\partial \langle N(\varepsilon) \rangle / \partial \varepsilon)$ is essentially Dirac's delta-function $\delta(\varepsilon - \varepsilon_F)$, so that the conductivity does not depend on temperature:¹⁵

$$\sigma = \frac{gq^2\tau}{(2\pi\hbar)^3} \frac{4\pi}{3} (8m\varepsilon_F^3)^{1/2} = \frac{q^2\tau}{m} \frac{g}{(2\pi\hbar)^3} \frac{4\pi}{3} (2m\varepsilon_F)^{3/2} = \frac{q^2\tau}{m} \frac{g}{(2\pi\hbar)^3} \frac{4\pi p_F^3}{3}. \quad (6.31)$$

But the last fraction in this product is just the volume of the Fermi sphere in the momentum space, so that the product of the last two fractions is the total number of quantum states filled at $T = 0$ (per unit volume), i.e. the total density $n \equiv N/V$ of electrons in the gas. Hence, Sommerfeld's result is reduced to the *Drude formula*,¹⁶

$$\sigma = \frac{q^2\tau}{m} n,$$

(6.32) Drude formula

which should be well familiar to the reader from an undergraduate physics course, with τ being a scale of time intervals between scattering events.

This calculation poses with an important conceptual question. The very structure of Eq. (30) implies that the only quantum states contributing to electric conductance are those where the derivative $(-\partial \langle N(\varepsilon) \rangle / \partial \varepsilon)$ is significant. At $T \ll \varepsilon_F$, these are the states at the very surface of the Fermi sphere's

¹⁴ Calculations for a classical gas (which are important, in particular, for most plasmas and non-degenerate semiconductors) are left for the reader – see the first assignment of Problem 2.

¹⁵ At least explicitly, because in some particle collision models, τ may be a function of temperature, which levels out only at some temperature much lower than ε_F .

¹⁶ It was derived in 1900 by P. Drude. Note that Drude also used the same arguments to derive a very simple (and very reasonable) approximation for the complex electric conductivity in the ac field of frequency ω : $\sigma(\omega) = \sigma(0)/(1 - i\omega\tau)$, with $\sigma(0)$ given by Eq. (32); sometimes the name “Drude formula” is used for this expression rather than for Eq. (32) – see Problem 1.

surface. On the other hand, the classical derivation of Eq. (32) involves *all* electrons.¹⁷ So, what exactly electrons are responsible for conductance: all of them, or only those on the Fermi surface?

For the resolution of this paradox, let us return to Eq. (22) and analyze the physical meaning of that result. For that, let us compare it with the following model distribution:

$$w_{\text{model}} \equiv w_0(\mathbf{r}, \mathbf{p} - \tilde{\mathbf{p}}, t), \quad (6.33)$$

where $\tilde{\mathbf{p}}$ is some constant, small vector, which describes a small shift of the unperturbed distribution w_0 in the momentum space as a whole. Performing the Taylor expansion of Eq. (33) in this small parameter, and keeping only two leading terms, we get

$$w_{\text{model}} \approx w_0(\mathbf{r}, \mathbf{p}, t) + \tilde{w}_{\text{model}}, \quad \tilde{w}_{\text{model}} = -\tilde{\mathbf{p}} \cdot \nabla_{\mathbf{p}} w_0(\mathbf{r}, \mathbf{p}, t). \quad (6.34)$$

Comparing the model perturbation with the first form of Eq. (22), we see that they coincide, provided that

$$\tilde{\mathbf{p}} = q\mathcal{E}\tau = \mathcal{F}\tau. \quad (6.35)$$

This means that Eq. (22) describes a small shift of the equilibrium distribution of electrons by $qE\tau$ (in p -space) along the direction of electric field,¹⁸ and gives the picture of the electron transport in a degenerate gas, shown in Fig. 4.

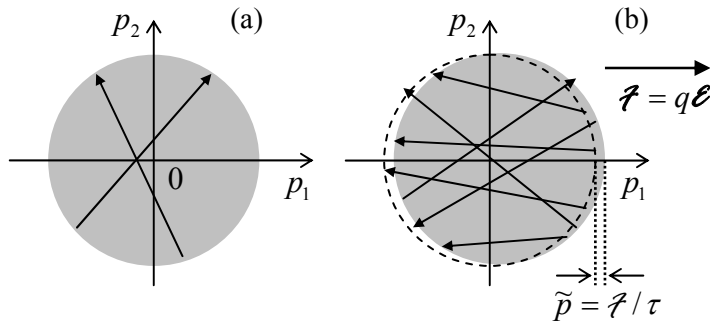


Fig. 6.4. Filling of momentum states in a degenerate electron gas: (a) in the absence and (b) in the presence of external electric field $\mathcal{E}$. Arrows show representative scattering events.

At $\mathcal{E} = 0$, the system is in equilibrium, so that the quantum states inside the Fermi sphere ($\mathbf{p} < \mathbf{p}_F$), are occupied, while those outside of it are empty (Fig. 4a). Electron scattering events happen only between states within a very thin layer ($|p^2/2m - \epsilon_F| \sim T$) at the Fermi surface, because only in this layer

¹⁷ As a reminder, here it is (see also EM Sec. 4.2): Let τ be the average time at which scattering causes a particle to loose all the deterministic component of its velocity, $\mathbf{v}_{\text{drift}}$, provided by electric field $\mathcal{E}$, on the top of electron's random thermal motion (which does not contribute to the net current). Using the 2nd Newton law to describe particle's acceleration by the field, $d\mathbf{v}_{\text{drift}}/dt = q\mathcal{E}/m$, we get $\langle \mathbf{v}_{\text{drift}} \rangle = \tau q\mathcal{E}/m$. Multiplying this result by the particle charge q and density $n = N/V$, we get the Ohm law $\mathbf{j} = \sigma\mathcal{E}$, with σ given by Eq. (32).

¹⁸ By the way, since the scale of the fastest change of w_0 in the momentum space is of the order of $\partial w_0/\partial p = (\partial w_0/\partial \epsilon)(d\epsilon/dp) \sim (1/T)v_F$, the linear approximation (34) is valid if $e\mathcal{E}\tau \ll T/v_F$, i.e. if $e\mathcal{E}l \ll T$, where $l \equiv v_F\tau$ is called the *mean free path*. This is the promised quantitative condition of the electric field smallness; since the left-hand part of the last inequality is just the average energy given to the particle by the electric field between two scattering events, the condition may be interpreted as the smallness of electron gas' "overheating" by the applied field. However, another condition is also necessary – see the last paragraph of this section.

the states are partially occupied, so that both components of the product $w(\mathbf{r}, \mathbf{p}, t)[1 - w(\mathbf{r}, \mathbf{p}', t)]$, mentioned in Sec. 1, do not vanish. These scattering events, on the average, do not change the equilibrium probability distribution, because they are uniformly spread over the Fermi surface.

In the instant the electric field has been turned on, it starts to accelerate all electrons in its direction, i.e. the whole Fermi sphere starts moving in the momentum space, along the field's direction in the real space. For elastic scattering events (with $|p'| = |p|$), this creates an addition of occupied states at the leading front of the accelerating sphere, and an addition of free states on its trailing edge (Fig. 4b). As a result, now there are more scattering events bringing electrons from the leading edge to the trailing edge of the sphere than in the opposite direction. This creates the average backflow of states occupancy in the momentum space. These two trends eventually cancel each other, and the Fermi sphere approaches a stationary (though not equilibrium!) state, with the shift (35) relatively to its thermal-equilibrium position.

Thus Fig. 4b presents a clear answer to the question which of the two different interpretations of the Drude formula is correct, and due to electrons' indistinguishability, the answer is: *either*. On one hand, we can look at the electric current as a result of shift (35) of *all* electrons in the momentum space. On the other hand, each filled quantum state deep inside the sphere gives exactly the same contribution into the net current density as it did without the field. All these internal contributions to the net current cancel each other, so that the applied field changes the situation only at the Fermi surface. Thus it is equally legitimate to say that *only the surface states* are responsible for the nonvanishing net current.¹⁹

Let me also mention the second paradox related to the Drude formula, which is often misunderstood (not only by students :-). As was emphasized above, τ is finite even at *elastic* scattering - that by itself does not change the total energy of the electron gas. The question is how can such scattering may be responsible for Ohmic resistivity $\rho \equiv 1/\sigma$, and hence for the Joule heat production, with power density $\mathcal{P}V = \mathbf{j} \cdot \mathcal{E} = \rho j^2$? The answer is that the Drude and Sommerfeld formulas describe just the “bottleneck” of the Joule heat formation. In the scattering picture (Fig. 4b) the elastically scattered electron states are predominantly located above the (shifted) Fermi surface, and eventually need to relax onto it via some inelastic process that releases their additional energy in the form of heat (in solid state materials, described by phonons – see Sec. 2.6). The rate and other features of these inelastic phenomena do not participate in the Drude formula directly, but for keeping the theory valid (in particular, keeping the probability distribution w close to its equilibrium value w_0), their intensity has to be sufficient to avoid gas overheating by the applied field. This gives an additional restriction on the simple theory described above. In some semiconductors, the charge carrier overheating effects, resulting in deviations from the Ohm law, i.e. from the linear relation (28) between $\mathbf{j}$ and $\mathcal{E}$, may be readily observed already at rather modest applied electric fields.

6.4. Electrochemical potential and the drift-diffusion equation

Now let us generalize our calculation to the case when transport takes place in the presence of a time-independent spatial gradient of the probability distribution, $\nabla w \neq 0$, caused for example by that of the particle concentration $n = N/V$ (and hence, according to Eq. (3.40), of the chemical potential μ),

¹⁹ So here, as it frequently happens in physics, formulas (or drawings, such as Fig. 4b) give a more clear and unambiguous description of the reality than words – the privilege lacked by many other scientific (and “scientific”) disciplines, frequently leading in unending, shallow verbal debates.

while still considering temperature T constant. For this generalization, we should just keep the second term in the left-hand part of Eq. (18). If the gradient of w is sufficiently small, we can repeat arguments of the last section and replace w with w_0 in this term as well. With the applied electric field $\mathcal{E}$ presented as $(-\nabla\phi)$, where ϕ is the electrostatic potential, Eq. (25) now becomes

$$\tilde{w} = \tau \mathbf{v} \cdot \left(\frac{\partial w_0}{\partial \varepsilon} q \nabla \phi - \nabla w_0 \right). \quad (6.36)$$

Since in any of distributions (20), $\langle N(\varepsilon) \rangle$ is a function of ε and μ only in combination $(\varepsilon - \mu)$, it obeys the following relation,

$$\frac{\partial \langle N(\varepsilon) \rangle}{\partial \mu} = - \frac{\partial \langle N(\varepsilon) \rangle}{\partial \varepsilon}. \quad (6.37)$$

Using this relation, the gradient of $w_0 \propto \langle N(\varepsilon) \rangle$ may be presented as²⁰

$$\nabla w_0 = - \frac{\partial w_0}{\partial \varepsilon} \nabla \mu, \quad \text{for } T = \text{const}, \quad (6.38)$$

so that Eq. (26) becomes

$$\tilde{w} = \tau \frac{\partial w_0}{\partial \varepsilon} \mathbf{v} \cdot (q \nabla \phi + \nabla \mu) = \tau \frac{\partial w_0}{\partial \varepsilon} \mathbf{v} \cdot q \nabla \Phi, \quad (6.39)$$

where the following sum,

$$\Phi \equiv \phi + \frac{\mu}{q}, \quad (6.40)$$

is called the *electrochemical potential*.²¹ Now repeating the calculation of the electric current, carried out in the last section, we get the following generalization of the Ohm law (28):

$$\mathbf{j} = \sigma (-\nabla \Phi) = \sigma \mathcal{E}, \quad (6.41)$$

where the *effective electric field* $\mathcal{E}$ is the (minus) gradient of the electrochemical potential, rather of the electrostatic potential:

$$\mathcal{E} \equiv -\nabla \Phi = \mathcal{E} - \frac{\nabla \mu}{q}. \quad (6.42)$$

The physics of this extremely important result²² may be explained in two ways. First, let us have a look at the energy spectrum of a uniform, degenerate Fermi gas confined in a volume of finite size. In order to ensure such a confinement, we need a piecewise-constant potential $U(\mathbf{r})$ - a “hard-wall, flat-

²⁰ Since we consider w_0 as a function of two *independent* arguments $\mathbf{r}$ and $\mathbf{p}$, taking its gradient, i.e. differentiation of this function over $\mathbf{r}$, does not involve its differentiation over the kinetic energy ε - which is a function of $\mathbf{p}$ only.

²¹ In electronic engineering literature, variable $q\Phi \equiv \mu + q\phi$, called the *local Fermi level*, is more frequently used.

²² Relation (42) does not include the phenomenological parameter τ of the relaxation-time approximation, so that it is more general than the RTA. Indeed, Eq. (42) is based on the relation between the second and third terms in the left-hand part of the rather general Eq. (10).

bottom potential well” – see Fig. 5a. (In a solid conductor, such profile is readily provided by the crystal lattice of positively charged ions of the crystal lattice.) The well should be of a sufficient depth $U_0 > \varepsilon_F \equiv \mu|_{T=0}$ in order to provide the confinement of the overwhelming majority of the particles, with energies below or slightly above the Fermi level ε_F . This means that there should be a substantial energy gap,

$$\psi \equiv U_0 - \mu \gg T, \quad (6.43)$$

between the Fermi energy of a particle inside the well, and its potential energy outside the well. (The latter value is usually called the *vacuum level*.) The difference defined by Eq. (43) is called the *workfunction*,²³ for most metals, its is between 4 and 5 eV, so that relation $\psi \gg T$ is well fulfilled for the room temperatures ($T \sim 0.025$ eV) - and actually for all temperatures up to material’s evaporation point.

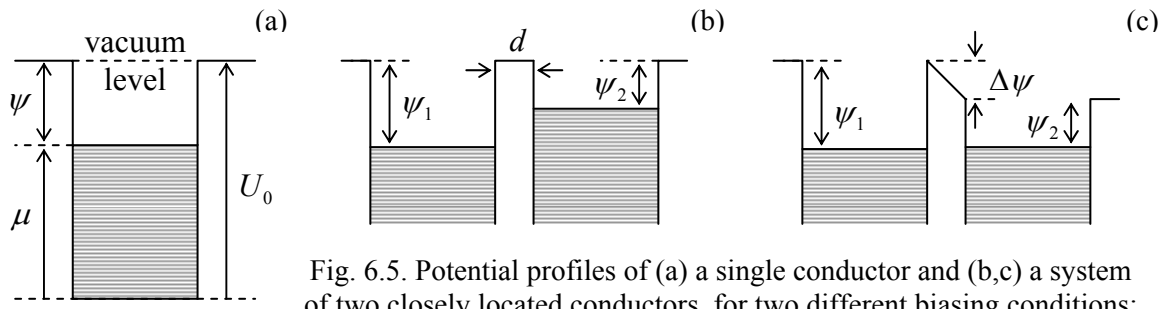


Fig. 6.5. Potential profiles of (a) a single conductor and (b,c) a system of two closely located conductors, for two different biasing conditions: (b) zero electrostatic field (“flat-band”), and (c) zero voltage $V \equiv \Delta\Phi$.

Now let us consider two conductors, with different values of ψ , separated by a small gap d – see Fig. 5b,c. Panel (b) shows the case when the electric field $\mathcal{E} = -\nabla\phi$ in the free-space gap between the conductors equals zero, i.e. their *electrostatic* potentials ϕ are equal.²⁴ If there is an opportunity for particles to cross the gap (e.g., by either the thermally-activated hopping over the potential barrier, discussed in Secs. 5.6-5.7, or quantum-mechanical tunneling through it), there will be an average flux of particles from the conductor with the higher Fermi level to that with the lower Fermi level,²⁵ because the chemical equilibrium requires their equality – see Secs. 1.5 and 2.7. If the particles have an electric charge (as electrons do), the equilibrium will be automatically achieved by them recharging the effective capacitor formed by the conductors, until the electrostatic energy difference $q\Delta\phi$ reaches the value reproducing that of the workfunctions (Fig. 5c). According to Eq. (43), at the recharging, sum $(\psi + \mu)$ of each conductor has to stay constant, so that for the equilibrium potential difference²⁶ we may write

$$q\Delta\phi = \Delta\psi = -\Delta\mu. \quad (6.44)$$

²³ Sometimes also called the “electron affinity”, though the latter term is mostly used for atoms and molecules.

²⁴ In semiconductor physics and engineering, the situation shown in Fig. 5b is called the *flat-band condition*, because in semiconductors, any electric field at the surface leads to *band bending* – a gradual spatial change of the background potential U_0 and hence of all energy band/gap edges. For a discussion of the band bending and its effects on semiconductor device operation, see, e.g., either Chapter 6 in J. Hook and H. Hall, *Solid State Physics*, 2nd ed. Wiley, 1991, or Chapter 3 in S. Sze, *Semiconductor Devices*, 2nd ed., Wiley, 2001.

²⁵ As measured from a common reference value, for example from the vacuum level.

²⁶ In physics literature, it is usually called the *contact potential difference*, while in electrochemistry (for which it is one of the key notions), the term *Volta potential* is more common.

At this equilibrium, the electric field in the gap between the conductors is

$$\mathcal{E} \equiv -\frac{\Delta\phi}{d}\mathbf{n} = \frac{\Delta\mu}{qd}\mathbf{n} = \frac{\nabla\mu}{q}; \quad (6.45)$$

in Fig. 5c the field is clearly visible as the tilt of the electric potential profile. Comparing Eq. (45) with definition (42) of the effective electric field $\mathcal{E}$, we see that the transport equilibrium, i.e. the absence of current, is achieved exactly when $\mathcal{E} = 0$, in accordance with Eq. (41).

Another interpretation of Eq. (41) may be achieved by modifying Eq. (38) for the particular case of a classical gas. Indeed, the gas' local density $n \equiv N/V$ obeys Eq. (3.32), which may be presented as

$$n(\mathbf{r}) = \text{const} \times \exp\left\{\frac{\mu(\mathbf{r})}{T}\right\}. \quad (6.46)$$

Taking the spatial gradient of the both parts of this relation (at constant T), we get

$$\nabla n = \text{const} \times \frac{1}{T} \exp\left\{\frac{\mu}{T}\right\} \nabla\mu = \frac{n}{T} \nabla\mu, \quad (6.47)$$

so that $\nabla\mu = (T/n)\nabla n$, and Eq. (41), with σ given by Eq. (32), may be recast as

$$\mathbf{j} = \sigma(-\nabla\Phi) = \frac{q^2\tau}{m}n\left(-\nabla\phi - \frac{1}{q}\nabla\mu\right) = q\frac{\tau}{m}(nq\mathcal{E} - T\nabla n). \quad (6.48)$$

Hence the current may be viewed as consisting of two independent parts: one due to the “usual” electric field $\mathcal{E} = -\nabla\phi$, and another due to the particle diffusion – see Eq. (5.118) and its discussion. This is exactly the physics of the “mysterious” term $\nabla\mu$ in Eq. (42), though it may be presented in the simple form (48) only in the classical limit.

Besides being very useful for practice,²⁷ Eq. (48) gives us a pleasant surprise. Namely, plugging it into the continuity equation for electric charge,

$$\frac{\partial(qn)}{\partial t} + \nabla \cdot \mathbf{j} = 0, \quad (6.49)$$

we get (after the division of all terms by $q\tau/m$) the so-called *drift-diffusion equation*:²⁸

Drift-
diffusion
equation

$$\frac{m}{\tau} \frac{\partial n}{\partial t} = \nabla(n\nabla U) + T\nabla^2 n, \quad \text{with } U \equiv q\phi. \quad (6.50)$$

Comparing it with Eq. (5.122), we see that the drift-diffusion equation is identical to the Smoluchowski equation,²⁹ if we identify ratio τ/m with mobility $\mu_m = 1/\eta$:

$$\frac{\tau}{m} \leftrightarrow \mu_m \equiv \frac{1}{\eta}, \quad (6.51)$$

²⁷ In particular, in physics of semiconductor devices, where electrons in the conduction band, and holes in the valence band, may be frequently treated as nearly-ideal classical gases.

²⁸ Sometimes this term is associated with Eq. (52).

²⁹ And hence, at negligible ∇U , identical to the diffusion equation (5.116).

and hence the following combination, $\tau T/m$, with the diffusion constant D – see (5.78). As a result, Eq. (48) is frequently rewritten as an expression for the *particle flow density* $\mathbf{j}_n \equiv n\mathbf{j}_w = \mathbf{j}/q$:

$$\mathbf{j}_n = n\mu_m q \mathcal{E} - D\nabla n. \quad (6.52)$$

This similarity may look surprising. Indeed, our (or rather Einstein's :-)) treatment of the Brownian motion in Chapter 5 was based on a strong hierarchy of the total system, consisting of a large “Brownian particle” in an environment of many smaller particles – “molecules”. On the other hand, in this chapter we are considering a gas of similar particles. Nevertheless, the equations describing the dynamics of their probability distribution, are the same – at least within the framework of the Boltzmann transport equation with the relaxation-time approximation (17) of the scattering integral.

The origin of this similarity is that Eq. (12) is applicable to Brownian particles as well, with each “scattering” event being the particle's hit by a random molecule. Since, due to the mass hierarchy, the particle momentum change at each such event is small, the scattering integral has to be local, i.e. depend only on w at the same momentum $\mathbf{p}$ as the left-hand part of the Boltzmann equation, so that the relaxation time approximation (17) is absolutely natural. But the same is true for collisions of similar particles, if they are dominated by small-angle scattering, as true, for example, for Coulomb scattering.³⁰

Returning to the electric field duality ($\mathcal{E} \leftrightarrow \mathcal{E}$), recovered in our analysis, it raises a natural question: which of these fields we are speaking about in the everyday and laboratory practice? Upon some contemplation, the reader should agree that most of our electric field measurements are done indirectly, by measuring corresponding voltages – with voltmeters. A vast majority of these instruments belong to the *electrodynamic* variety that is based on the measurement of a small current flowing through the voltmeter. As Eq. (41) shows, electrodynamic voltmeters measure the *electrochemical* potential difference $\Delta\Phi$. However, there exist a rare breed of *electrostatic* voltmeters (also called “electrometers”) that measure the *electrostatic* potential difference $\Delta\phi$ between two conductors. One way to implement such an instrument is to use a usual, electrodynamic voltmeter, but with the reference point set at the flat-band condition (Fig. 5b) between the conductors. This condition may be detected by vanishing electric charge on the adjacent surfaces of the conductors, and hence by the absence of its modulation in time, caused by a specially arranged periodic variation of the distance between the surfaces. Another (less sensitive but also less invasive) way to detect the flat-band condition is to measure the voltage at which the force of electrostatic interaction between two conductors, which is proportional to $\mathcal{E}^2 \propto (\Delta\phi)^2$, vanishes.

6.5. Thermoelectric effects

Now let us extend our analysis even further, to the effects of a finite (though small) temperature gradient. Again, since for any of statistics (20), the average occupancy $\langle N(\varepsilon) \rangle$ is a function of just one combination of all its arguments, $\xi \equiv (\varepsilon - \mu)/T$, its partial derivatives obey not only Eq. (37), but also the following relation:

$$\frac{\partial \langle N(\varepsilon) \rangle}{\partial T} = -\frac{\varepsilon - \mu}{T^2} \frac{\partial \langle N(\varepsilon) \rangle}{\partial \xi} = \frac{\varepsilon - \mu}{T} \frac{\partial \langle N(\varepsilon) \rangle}{\partial \mu}. \quad (6.53)$$

³⁰ See, e.g., CM Sec. 3.7.

As a result, Eq. (38) is generalized as

$$\nabla w_0 = -\frac{\partial w_0}{\partial \varepsilon} \left(\nabla \mu + \frac{\varepsilon - \mu}{T} \nabla T \right), \quad (6.54)$$

giving the following generalization of Eq. (39):

$$\tilde{w} = \tau \frac{\partial w_0}{\partial \varepsilon} \mathbf{v} \cdot \left(q \nabla \Phi + \frac{\varepsilon - \mu}{T} \nabla T \right). \quad (6.55)$$

Now, repeating the current density calculation, we get a result which is traditionally presented as

$$\mathbf{j} = \sigma (-\nabla \Phi) + \sigma \mathcal{S} (-\nabla T), \quad (6.56)$$

where constant $\mathcal{S}$, called the *Seebeck coefficient*³¹ (or the “thermoelectric power”, or just “thermopower”) is defined by the following relation:

Seebeck
coefficient

$$\sigma \mathcal{S} = \frac{gq\tau}{(2\pi\hbar)^3} \frac{4\pi}{3} \int_0^\infty (8m\varepsilon^3)^{1/2} \frac{(\varepsilon - \mu)}{T} \left(-\frac{\partial \langle N(\varepsilon) \rangle}{\partial \varepsilon} \right) d\varepsilon. \quad (6.57)$$

Working out this integral for the most important case of a degenerate Fermi gas, with $T \ll \varepsilon_F$, we have to be careful, because the center of the sharp peak of the last factor under the integral coincides with the zero point of the previous factor, $(\varepsilon - \mu)/T$. This uncertainty may be resolved using the Sommerfeld expansion formula (3.59). Indeed, for a smooth function $f(\varepsilon)$ defined by Eq. (3.60), so that $f(0) = 0$, we may use (3.61) to rewrite the formula as

$$\int_0^\infty f(\varepsilon) \left(-\frac{\partial \langle N(\varepsilon) \rangle}{\partial \varepsilon} \right) d\varepsilon = f(\mu) + \frac{\pi^2}{6} T^2 \frac{d^2 f(\varepsilon)}{d\varepsilon^2} \Big|_{\varepsilon=\mu}. \quad (6.58)$$

In particular, for integral (57), we may take $f(\varepsilon) \equiv (8m\varepsilon^3)^{1/2}(\varepsilon - \mu)/T$. (Evidently, for this function, condition $f(0) = 0$ is satisfied.) Then $f(\mu) = 0$, $d^2 f/d\varepsilon^2|_{\varepsilon=\mu} = 3(8m\mu)^{1/2}/T \approx 3(8m\varepsilon_F)^{1/2}/T$, and Eq. (57) yields

$$\sigma \mathcal{S} = \frac{gq\tau}{(2\pi\hbar)^3} \frac{4\pi}{3} \frac{\pi^2}{6} T^2 \frac{3(8m\varepsilon_F)^{1/2}}{T}. \quad (6.59)$$

Comparing the result with Eq. (31), for constant $\mathcal{S}$ we get a simple expression independent of τ .³²

$$\mathcal{S} = \frac{\pi^2}{2q} \frac{T}{\varepsilon_F} = \frac{c_V}{q}, \quad (6.60)$$

where $c_v \equiv C_V/N$ is the heat capacity of the gas per unit particle, given by Eq. (3.70).

³¹ Named after T. Seebeck who experimentally discovered, in 1821 (independently of J. Peltier), the effect expressed by Eq. (62).

³² Again, such independence infers that Eq. (60) should have a broader validity than in our simple model of an isotropic gas. This is indeed the case: at $T \ll \varepsilon_F$, this result turns out to be valid for any form of the Fermi surface, and for any dispersion law $\varepsilon(\mathbf{p})$.

In order to understand the physical meaning of the Seebeck coefficient, it is sufficient to consider a conductor carrying no current. For this case, Eq. (56) yields

$$\nabla(\Phi + \mathcal{S}T) = 0.$$

(6.61)

Seebeck effect

Thus, the temperature gradient creates the oppositely directed gradient of the effective electric potential Φ , i.e. the effective field $\mathcal{E}$ defined by Eq. (42). This is the *Seebeck effect*. Figure 6 shows the standard way of its measurement, using a usual (electrodynamic) voltmeter that measures the difference of potentials Φ , and a connection (in this context, called *thermocouple*) of two different materials, with different coefficients $\mathcal{S}$. Integrating Eq. (61) around the loop from point A to point B , and neglecting the temperature drop across the voltmeter, we get the following simple expression for the thermally-induced difference of the electrochemical potential, frequently also called the either the *thermoelectric power* or “thermo e.m.f.”:

$$\begin{aligned} \mathcal{V} \equiv \Phi_B - \Phi_A &= \int_A^B \nabla \Phi \cdot d\mathbf{r} = - \int_A^B \mathcal{S} \nabla T \cdot d\mathbf{r} = -\mathcal{S}_1 \int_{A'}^{A''} \nabla T \cdot d\mathbf{r} - \mathcal{S}_2 \left(\int_{A''}^B \nabla T \cdot d\mathbf{r} + \int_A^{A'} \nabla T \cdot d\mathbf{r} \right) \\ &= -\mathcal{S}_1(T'' - T') - \mathcal{S}_2(T' - T'') = (\mathcal{S}_1 - \mathcal{S}_2)(T' - T''). \end{aligned} \quad (6.62)$$

(Note that according to Eq. (62), any attempt to measure such voltage across any two points of a *uniform* conductor would give results depending on the voltmeter lead materials, due to the unintentional gradient of temperature in them.)

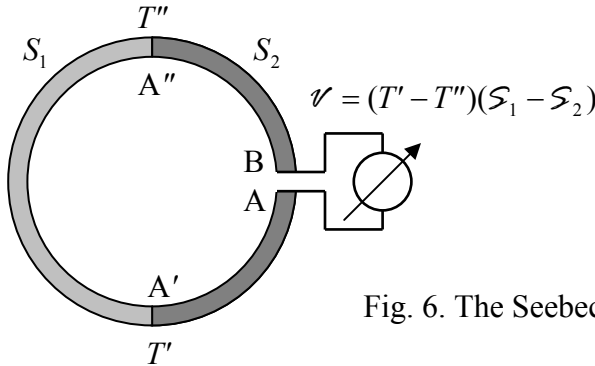


Fig. 6. The Seebeck effect in a thermocouple.

Using thermocouples is a popular, inexpensive method of temperature measurement – especially in the few-hundred-°C range (where gas- and fluid-based thermometers are not too practicable), if a 1°C-scale accuracy is sufficient. The “responsivity” ($\mathcal{S}_1 - \mathcal{S}_2$) of a typical popular thermocouple, chromel-constantan,³³ is about 70 $\mu\text{V}/^\circ\text{C}$. In order to understand why typical values of $\mathcal{S}$ are so small, let us discuss Seebeck effect’s physics. Superficially, it is very simple: particles, heated by an external source, diffuse from it toward the colder parts of the conductor, carrying electrical current with them if they are charged. However, this naïve argument neglects the fact that at $\mathbf{j} = 0$, there should be no total flow of particles. For a more accurate interpretation, note that the Seebeck effect is described by the factor $(\varepsilon - \mu)/T$ in integral (57), which changes sign at the Fermi surface, i.e. at the same energy where the term $(-\partial\langle N(\varepsilon) \rangle / \partial \varepsilon)$, describing the state availability for transport (due to their intermediate occupancy

³³ Both these materials are *alloys*, i.e. solid solutions: chromel is 10% chromium in 90% nickel, while constantan is 45% nickel and 55% copper.

$0 < \langle N(\varepsilon) \rangle < 1$), reaches its peak. The only reason why that integral does not vanish completely, and hence $\mathcal{S} \neq 0$, is the growth of first factor under the integral (which describes the number of available quantum states) with ε , so the hotter particles (with $\varepsilon > \mu$) are more numerous and carry more heat than the colder ones.

The Seebeck effect is of course not the only result of temperature gradient; the same diffusion of hotter particles also causes a flow of *heat* from the region of higher T to those with lower T , i.e. the effect of *thermal conductivity*, well known from our everyday practice. The heat (i.e. thermal energy) flow density may be calculated similarly to that of the electric current – see Eq. (26), with the natural replacement of the electric charge q of each particle with the thermal energy ($\varepsilon - \mu$) of its state:³⁴

$$\mathbf{j}_h = \int (\varepsilon - \mu) \mathbf{v} w d^3 p. \quad (6.63)$$

Again, at equilibrium ($w = w_0$) the heat flow vanishes, so that w may be replaced with its perturbation $\tilde{w}$, which already has been calculated – see Eq. (55). The substitution of that expression into Eq. (63), and its transformation exactly similar to the one performed above for the electric current $\mathbf{j}$, yields³⁵

$$\mathbf{j}_h = \sigma \Pi (-\nabla \Phi) + \kappa (-\nabla T), \quad (6.64)$$

with coefficients Π and κ defined by equalities

$$\sigma \Pi = \frac{g q \tau}{(2\pi\hbar)^3} \frac{4\pi}{3} \int_0^\infty (8m\varepsilon^3)^{1/2} (\varepsilon - \mu) \left(-\frac{\partial \langle N(\varepsilon) \rangle}{\partial \varepsilon} \right) d\varepsilon, \quad (6.65)$$

$$\kappa = \frac{g \tau}{(2\pi\hbar)^3} \frac{4\pi}{3} \int_0^\infty (8m\varepsilon^3)^{1/2} \frac{(\varepsilon - \mu)^2}{T} \left(-\frac{\partial \langle N(\varepsilon) \rangle}{\partial \varepsilon} \right) d\varepsilon. \quad (6.66)$$

Besides the missing factor T in the denominator, integral in Eq. (65) is the same as in Eq. (57), so that constant Π (called the *Peltier coefficient*), is simply and fundamentally related to the Seebeck coefficient:³⁶

$$\Pi = \mathcal{S} T. \quad (6.67)$$

Peltier
coefficient
and thermal
conductivity

Π vs. $\mathcal{S}$

³⁴ One more way to look at Eq. (63) is as at the difference between the total energy flow density, $\mathbf{j}_e = \int \varepsilon \mathbf{v} w d^3 p$, and the product of a constant (μ) by the particle flow density, $\mathbf{j}_n = \int \mathbf{v} w d^3 p = \mathbf{j}/q$.

³⁵ The expression given by the second term of this relation, $\mathbf{j}_h' = -\kappa \nabla T$, is much more general than our analysis: for small temperature gradients it is valid in virtually any medium – for example, in insulators, where the first term of Eq. (64) vanishes. (In the general case, the thermal conductivity κ is of course different from that given by Eq. (66).) As a result, this relation has its own name – the *Fourier law*, because it has been first suggested by the same universal genius J.-B. J. Fourier – who has not only developed such a key mathematical tool as the Fourier series, but also discovered what is now called the greenhouse effect!

³⁶ The simplicity of this relation (first discovered experimentally in 1854 by W. Thompson, a.k.a. Lord Kelvin) is not occasional. This is one of fundamental *Onsager reciprocal relations* between kinetic coefficients (L. Onsager, 1931), which are model-independent, i.e. valid within very general assumptions. Unfortunately, I have no time left for a discussion of this interesting topic, and have to refer the interested reader, for example, to Sec. 120 in L. Landau and E. Lifshitz, *Statistical Physics*, 3rd ed., Pergamon, 1980. Note, however, that the range of validity of the Onsager relations is still debated – see, e.g., K.-T. Chen and P. Lee, *Phys. Rev. B* **79**, 18 (2009).

On the other hand, integral (66) may be readily calculated, for the most important case of a degenerate Fermi gas, using the Sommerfeld expansion (58) with $f(\varepsilon) \equiv (8m\varepsilon^3)^{1/2}(\varepsilon - \mu)^2/T$, for which $f(\mu) = 0$ and $d^2f/d\varepsilon^2|_{\varepsilon=\mu} = 2(8m\mu^3)^{1/2}/T \approx 2(8m\varepsilon_F^3)^{1/2}/T$, so that

$$\kappa = \frac{g\tau}{(2\pi\hbar)^3} \frac{4\pi}{3} \frac{\pi^2}{6} T^2 \frac{2(8m\varepsilon_F^3)^{1/2}}{T}. \quad (6.68)$$

Comparing the result with the first form of Eq. (31), we get the so called *Wiedemann-Franz law*³⁷

$$\kappa = \frac{\pi^2}{3} \frac{T}{q^2} \sigma. \quad (6.69) \quad \text{Wiedemann-Franz law}$$

This relation between the electric conductivity σ and *thermal conductivity* κ is more general than our formal derivation might imply. Indeed, it is straightforward to show that the Wiedemann-Franz law is also valid for an arbitrary dispersion law anisotropy (i.e. arbitrary Fermi surface shape) and, moreover, well beyond the relaxation-time approximation. (For example, it is also valid for scattering integral (12) with an arbitrary angular dependence of rate Γ , provided that scattering is elastic.) Experiments show that the law is well obeyed by most metals, but only at relatively low temperatures $T \ll T_D$, when the thermal conductance due to electrons is well above the one due to lattice vibrations, i.e. phonons – see Sec. 2.6. (Note also that Eq. (69) is *not* valid for classical gases – see Problem 2.)

Now let us discuss the less evident, first term of Eq. (64). It describes the so-called *Peltier effect*, which may be measured in the geometry similar to that shown in Fig. 6, but driven by an external voltage source – see Fig. 7.

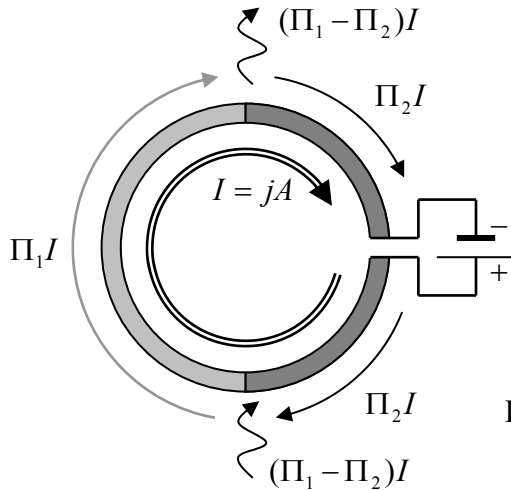


Fig. 7. The Peltier effect.

The voltage drives certain dc current $I = jA$ (where A is conductor's cross-section area), necessarily the same in the whole loop. However, according to Eq. (64), if materials 1 and 2 are

³⁷ It was named after G. Wiedemann and R. Franz who noticed the constancy of ratio κ/σ for various materials, at the same temperature, as early as in 1853. The direct proportionality of the ratio to the absolute temperature was noticed by L. Lorenz in 1872. Due to this contribution, the Wiedemann-Franz law is frequently presented as $\kappa/\sigma = LT$, where constant L , called the *Lorenz number*, in SI units is close to $2.45 \times 10^{-8} \text{ W}\cdot\Omega/\text{K}^2$. Theoretically, Eq. (69) was derived in 1928 by A. Sommerfeld.

different, power $\mathcal{P} = j_H A$ of the heat flow is different in two parts of the loop. Indeed, if the whole system is kept at the same temperature ($\nabla T = 0$), integration of the equation over the cross-section yields

$$\frac{(\mathcal{P})_{1,2}}{I} = \frac{(j_h)_{1,2}}{j} = \frac{(\sigma\Pi)_{1,2}}{\sigma_{1,2}} = \Pi_{1,2}. \quad (6.70)$$

This means that in order to sustain the constant temperature, the following power difference,

Peltier
effect

$$\Delta\mathcal{P} = (\Pi_1 - \Pi_2)I, \quad (6.71)$$

has to be extracted from one junction of the two materials, and inserted into another junction. If a constant temperature is not maintained, the former junction is heated, while the latter one is cooled (on the top of the bulk, Joule heating), thus implementing a *thermoelectric heat pump / refrigerator*. Such refrigerators, with no moving parts and gas/fluid materials, are very convenient for modest (by a few tens °C) cooling of relatively small components of various systems - from sensitive radiation detectors in spacecraft, all the way to cold drinks in vending machines. It is straightforward to use above formulas to show that the efficiency of active materials used in such thermoelectric refrigerators may be characterized by the following dimensionless figure-of-merit,

$$ZT \equiv \frac{\sigma\mathcal{S}^2}{\kappa} T. \quad (6.72)$$

For the best thermoelectric materials found so far, ZT is in the range from 2 to 3, providing the coefficient of performance, defined by Eq. (1.69), of the order of 0.5 - a few times lower than that of traditional, mechanical refrigerators. The search for composite materials (including those with nanoparticles) with higher values of ZT is one of very active fields of applied solid state physics.³⁸

Let me finish this chapter (and this course, and this series :-)) by emphasizing again that due to time/space restrictions I was able to barely scratch the surface of physical kinetics.³⁹

6.6. Exercise problems

6.1. Use the relaxation-time approximation of the Boltzmann equation to prove the Drude formula for the complex conductivity at frequency ω ,

$$\sigma(\omega) = \frac{\sigma(0)}{1 - i\omega\tau},$$

where $\sigma(0)$ is the dc conductivity given by Eq. (6.30) of the lecture notes, and give a physical interpretation of the formula.

³⁸ See, e.g., D. Rowe (ed.), *Thermoelectrics Handbook: Macro to Nano*, CRC Press, 2005.

³⁹ A much more detailed coverage of this important part of physics may be found, for example, in the textbook by L. Pitaevskii and E. Lifshitz, *Physical Kinetics*, Butterworth-Heinemann, 1981. A detailed discussion of its applications to mechanical engineering may be found, e.g., in T. Bergman *et al.*, *Fundamentals of Heat and Mass Transfer*, 7th ed., Wiley, 2011.

6.2. Use the variable separation method to calculate the time evolution of the particle density distribution in space, provided that at $t = 0$, the particles are released from their uniform distribution in a wide box of thickness $2a$:

$$n = \begin{cases} n_0, & \text{for } -a \leq x \leq +a, \\ 0, & \text{otherwise.} \end{cases}$$

6.3. For the 1D version of the diffusion equation (i.e. of the drift-diffusion equation (6.50) with $\tau T/m \equiv D$, and without the drift-inducing field, $\nabla U = 0$),

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}, \quad \text{for } -\infty < x < +\infty,$$

find an appropriate spatial-temporal Green's function, and use it to solve the previous problem.

6.4.* Calculate the electric conductance of a narrow, uniform conducting channel between two bulk conductors, in the low-voltage and low-temperature limit, neglecting the electron interaction and scattering inside the channel.

6.5. Calculate the electric conductivity σ , the thermal conductivity κ , as well as the thermoelectric coefficients $\mathcal{S}$ and Π , for a classical, ideal gas of electrically charged particles. Compare the results with those for the degenerate Fermi gas, derived in the lecture notes.

6.6. Derive a partial differential equation describing the time evolution of temperature distribution in a medium with negligible thermal expansion and with temperature-independent specific heat c_V and thermal conductivity κ , given by the Fourier law

$$\mathbf{j}_h = -\kappa \nabla T.$$

6.7. Use the equation derived in the previous problem to calculate the time evolution of temperature in the center of a uniform solid sphere of radius R , initially heated to temperature T_i , and at $t = 0$ placed into a heat bath that keeps its surface at temperature T_0 .

6.8. Suggest a reasonable definition of the entropy production rate (per unit volume), and calculate this rate for a stationary thermal conduction, assuming that it obeys the Fourier law, in a material with negligible thermal expansion. Give a physical interpretation of the result. Does the stationary temperature distribution in a sample correspond to the minimum of the total entropy production in it?